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Chain Transfer Processes in Single-Site Olefin Polymerization:  
Effects of Organosilanes and Amines as Chain Transfer Agents

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## ABSTRACT

Chain Transfer Processes in Single-Site Olefin Polymerization:  
Effects of Organosilanes and Amines as Chain Transfer Agents

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Alkenylsilanes of varying chain lengths are investigated as simultaneous chain transfer agents + comonomers in organotitanium-mediated olefin polymerization processes. Ethylene + alkenylsilane polymerizations were carried out with activated  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}^t\text{Bu})\text{TiMe}_2$  and  $(\mu\text{-CH}_2\text{CH}_2\text{-3,3'})\{(\eta^5\text{-indenyl})[1\text{-Me}_2\text{Si}(^t\text{BuN})]\}_2\text{Ti}_2\text{Me}_4$  precatalysts. Alkenylsilane incorporation levels follow the trend  $\text{C}_8\text{H}_{15}\text{SiH}_3 < \text{C}_6\text{H}_{11}\text{SiH}_3 \approx \text{C}_4\text{H}_7\text{SiH}_3 < \text{C}_3\text{H}_5\text{SiH}_3$ . Long-chain branching levels versus total branch content follow the trend  $\text{C}_3\text{H}_5\text{SiH}_3 < \text{C}_4\text{H}_7\text{SiH}_3 \approx \text{C}_6\text{H}_{11}\text{SiH}_3 \approx \text{C}_8\text{H}_{15}\text{SiH}_3$ . Ti nuclearity influences silanolytic chain transfer processes, with binuclear systems exhibiting sublinear relationships between  $M_n$  and  $[\text{alkenylsilane}]^{-1}$  for allylsilane and 3-butenylsilane, and superlinear relationships between  $M_n$  and  $[\text{alkenylsilane}]^{-1}$  for 5-hexenylsilane and 7-octenylsilane. For mononuclear Ti systems, alkenylsilanes up to  $\text{C}_6$  demonstrate linear relationships between  $M_n$  and  $[\text{alkenylsilane}]^{-1}$ , consistent with a silanolytic chain termination mechanism.

Organosilane reagents are introduced into organotitanium-mediated styrene polymerizations to produce atactic polystyrene. The resulting polymers were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, GPC, and DSC. High activities (up to  $10^6$  g polymer/ (mol Ti • h)) and narrow polydispersities are observed in the polymerization process. Previously recognized  $\text{CGCTiMe}_2$

systems having marginal styrene homopolymerization activity are shown to be up to 3 orders of magnitude more active upon addition of organosilane. Control experiments indicate that the Si–H moiety is significant in the organotitanium-mediated styrene polymerization process.

Amines of varying Brønsted acidity and steric encumbrance are investigated as chain-transfer agents in organolanthanide-mediated olefin polymerization processes. Ethylene homopolymerizations are carried out with activated  $\text{Cp}'_2\text{LnCH}(\text{Si}(\text{CH}_3)_3)_2$  ( $\text{Cp}' = \eta^5\text{-Me}_5\text{C}_5$ ); Ln = La, Sm, Y, Lu precatalysts in the presence of primary and secondary amines. Amine chain transfer efficiency follows the trend  $\text{C}_6\text{H}_5\text{NH}_2 \approx \text{C}_3\text{H}_7\text{NH}_2 \ll (\text{Si}(\text{CH}_3)_3)_2\text{NH} \approx {}^{\text{sec}}\text{Bu}_2\text{NH} < N\text{-}^t\text{Bu}(\text{Si}(\text{CH}_3)_3)\text{NH} \approx {}^i\text{Pr}_2\text{NH} < (\text{C}_6\text{H}_{11})_2\text{NH}$  to yield polyethylenes of the structure  $\text{H}(\text{CH}_2\text{CH}_2)_n\text{NRR}'$ . Under the conditions investigated, primary amines are the most stable towards  $\text{Cp}'_2\text{La}$ -mediated polymerizations, affording no detectable insertion products, while secondary amines produce mono-ethylene insertion products, amine-capped oligoethylenes, and high molecular weight amine-terminated polyethylenes. Here, protonolysis appears to be the dominant chain-transfer pathway. Organotitanium-mediated ethylene and propylene polymerizations in the presence of secondary amines result in modest polymerization rates with activities of  $10^4$  g polymer/(mol of Ti • atm ethylene • h).

To Zachary and the Amin Family

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## Chapter 4

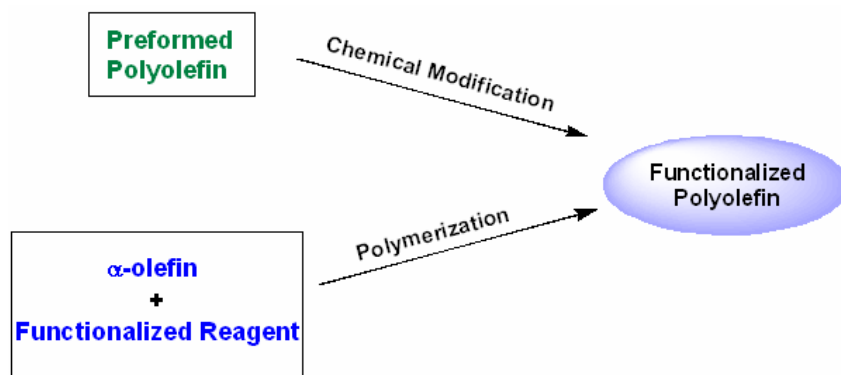
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## **CHAPTER 1**

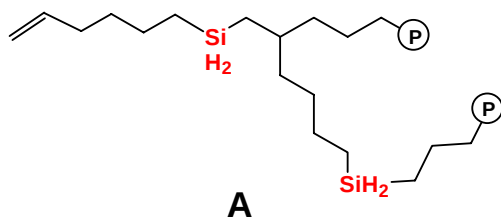
Introduction: Versatile Routes to In Situ Polyolefin Functionalization with Heteroatoms.  
Catalytic Chain Transfer

Chain-transfer agents, defined as chemical reagents which both terminate and facilitate reinitiation of polymer chain growth, can efficiently control molecular weight and concomitantly introduce chemical functionality in polymer chains. Functionalized polyolefins<sup>1</sup> have many attractions versus non-functionalized polyolefins, including but not limited to, increased adhesion, paintability, and compatibility with diverse, more polar materials.<sup>2</sup> Over the past decade, there have been a number of advances in methodologies for the functionalization of polyolefins.<sup>1</sup> The two conventional pathways by which polyolefin functionalization can be achieved are: 1) post-polymerization modification and 2) direct catalytic introduction of functional groups (Scheme 1-1). In general, post-polymerization modification<sup>3</sup> of pre-synthesized polyolefins avoids the issues of catalyst functional group tolerance and catalyst poisoning. However, the unreactive nature of hydrocarbon polymers leads to difficult chemical modifications with potentially harsh reaction conditions and a general lack of selectivity during the functionalization process. In contrast, selective and catalytic introduction of functional groups into polymerization processes offers the advantage of a controlled one-pot in situ synthesis. One effective catalytic method involves copolymerization with polar comonomers.<sup>4</sup> However, this approach is generally restricted to less oxophilic late-transition metal catalysts, which are more tolerant to polar functional groups, and turnover frequencies tend to be modest. Another catalytic approach, which is the focus of this thesis, involves incorporation of chain-transfer agents into olefin polymerization processes. Despite the potential disadvantages of catalyst poisoning or deactivation, diverse classes of chain-transfer agents and mechanisms have been discovered and shown to enable efficient, catalytic routes to functionalized polyolefins.

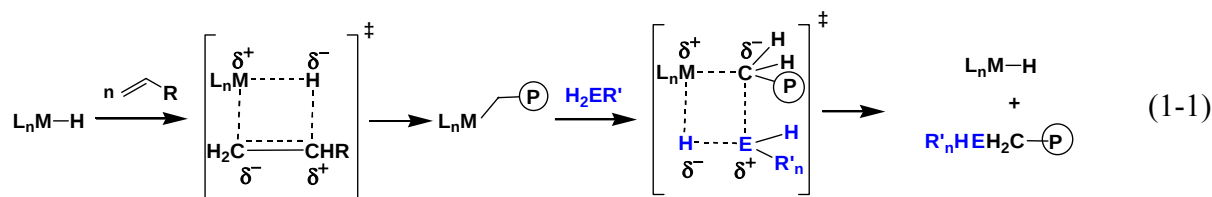
**Scheme 1-1.** Pathways for Polyolefin Functionalization.



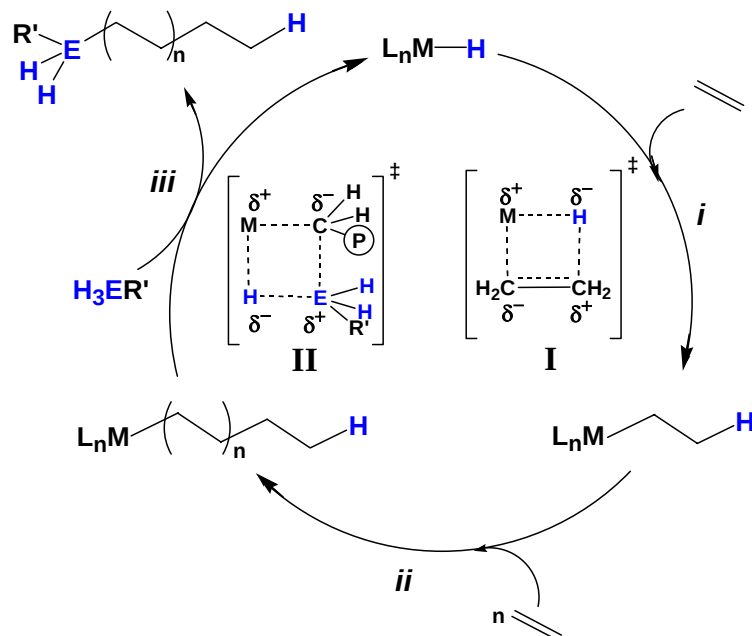
There are two distinct classes of chain-transfer agents, electron-deficient/neutral and electron-rich, that proceed via distinctly different pathways (Schemes 1-2 and 1-3, respectively). Electron-deficient/neutral chain-transfer agents such as silanes,<sup>5</sup> boranes,<sup>6</sup> and alanes<sup>7,8,9,10, 11,12</sup> have been extensively investigated in single-site catalyzed olefin polymerization systems<sup>13</sup> with the goal of efficiently producing polyolefins having heteroatom-functionalized chain ends (Scheme 1-2, Figure 1-1). Furthermore, borane-functionalized comonomers have also successfully been implemented in a variety of copolymerization processes<sup>14</sup> to catalytically access polymers with functionalized side-chains (e.g., **A**; P = polymer fragment). In contrast to



the above results with electron-deficient groups 3 and 4 hydrides, electron-rich groups 5 and 6 hydride chain-transfer agents such as phosphines<sup>15</sup> have also been effectively implemented in organolanthanide-mediated polymerization systems, but proceed mechanistically via a completely different pathway (Scheme 1-3). Thus, electron-deficient/neutral and electron-rich chain-transfer agents catalytically functionalize polyolefin chain-ends in complementary ways: one via a metal hydride-based, M-C/E-H transposition cycle, the other via a metal-element-based, olefin insertion/alkyl protonolysis cycle (eqs 1-1 and 1-2, respectively).

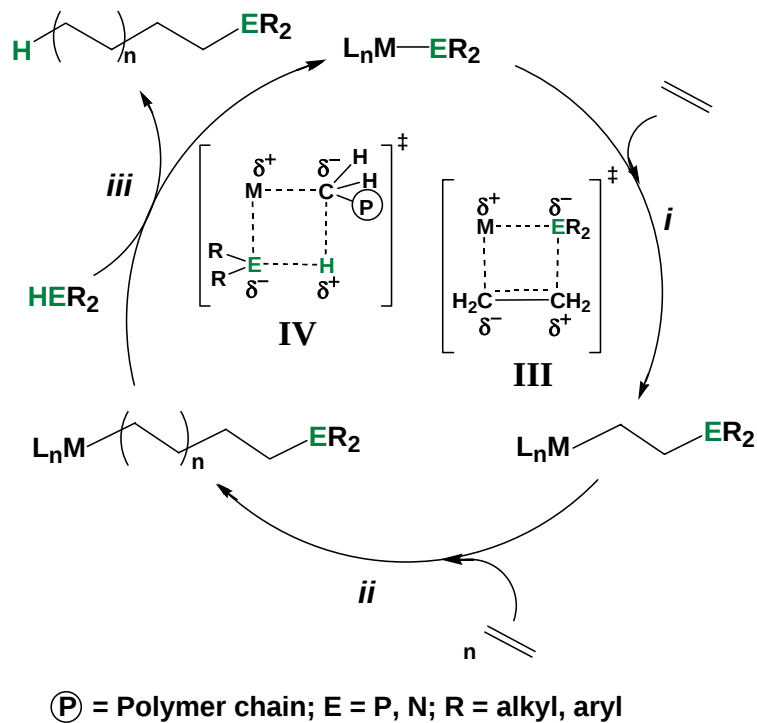


**Scheme 1-2.** Proposed Catalytic Cycle for Single-Site-Mediated Olefin Polymerization in the Presence of Electron-Deficient Chain Transfer Agents

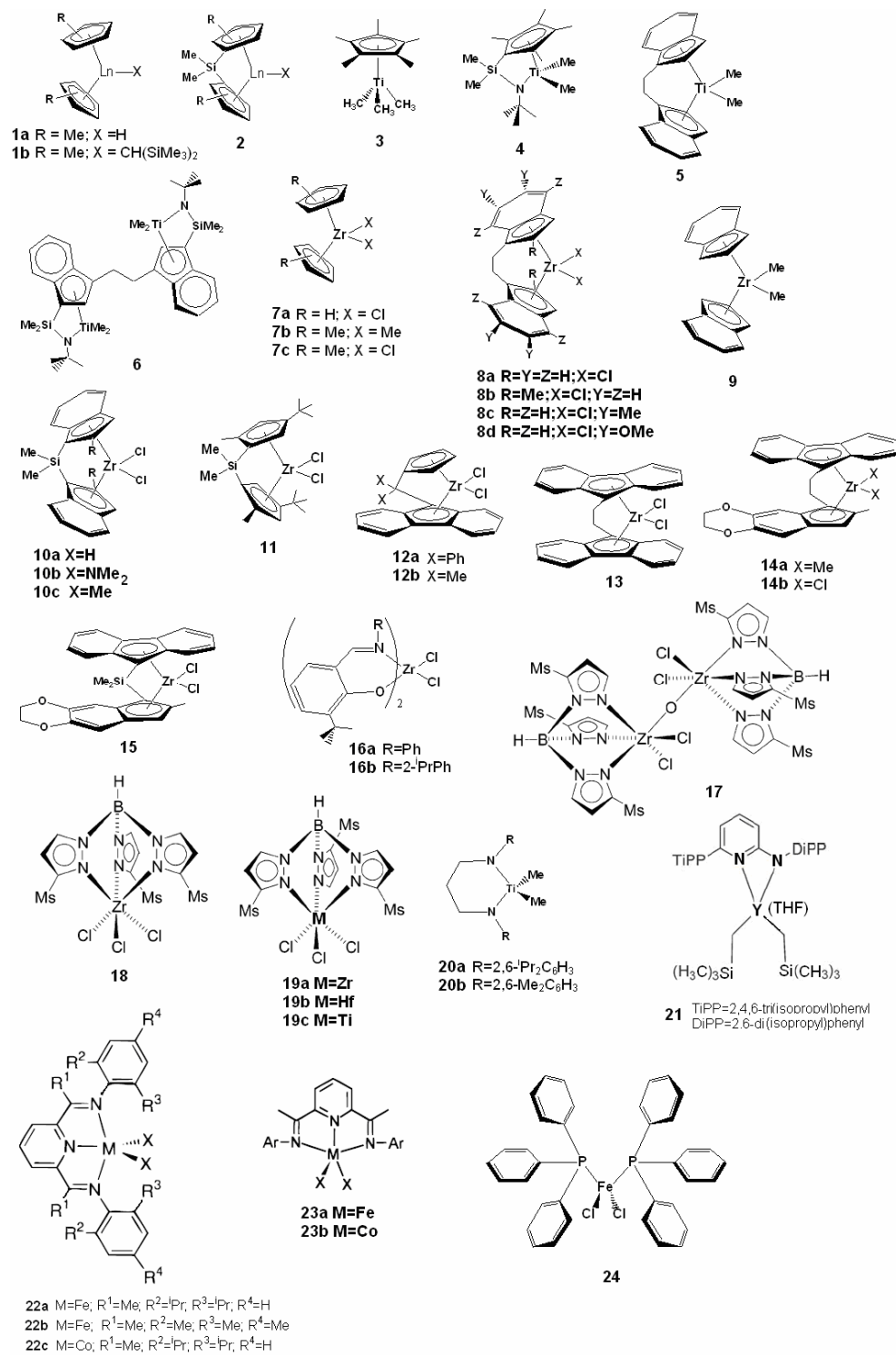


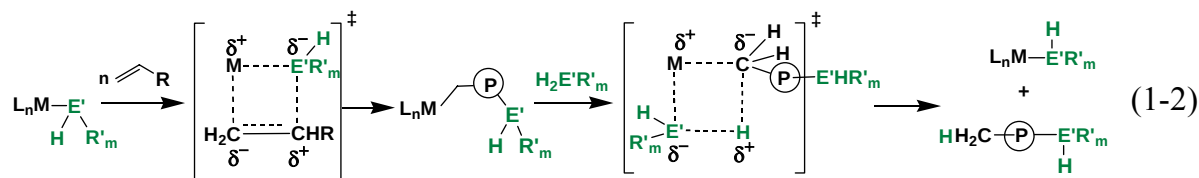
Ⓟ = Polymer chain; E = Si, B, Al; R' = alkyl, aryl

**Scheme 1-3.** Proposed Catalytic Cycle for Single-Site-Mediated Olefin Polymerization in the Presence of Electron-Rich Chain Transfer Agents



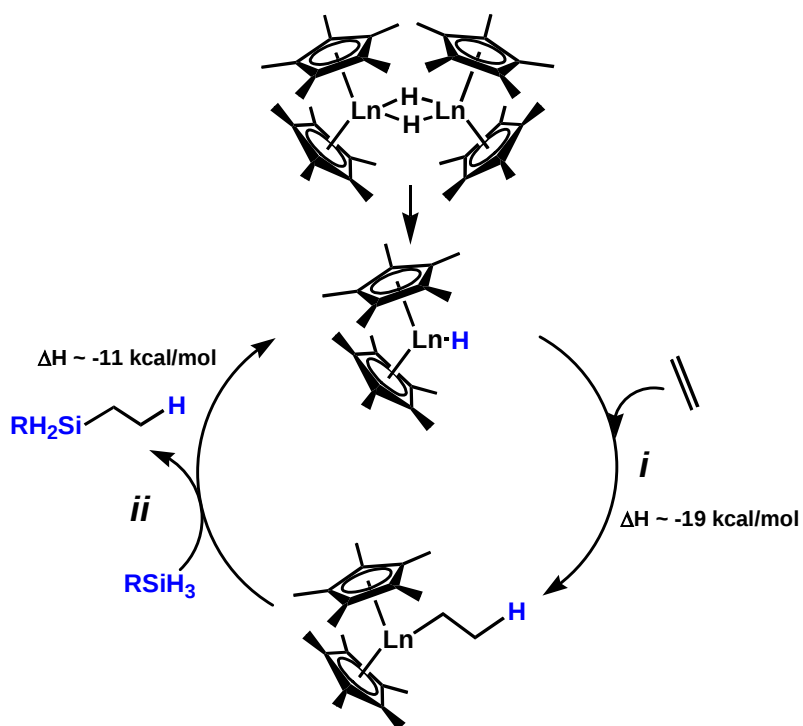
**Figure 1-1.** Representative single-site catalysts used for olefin polymerization in the presence of electron-deficient chain-transfer agents.



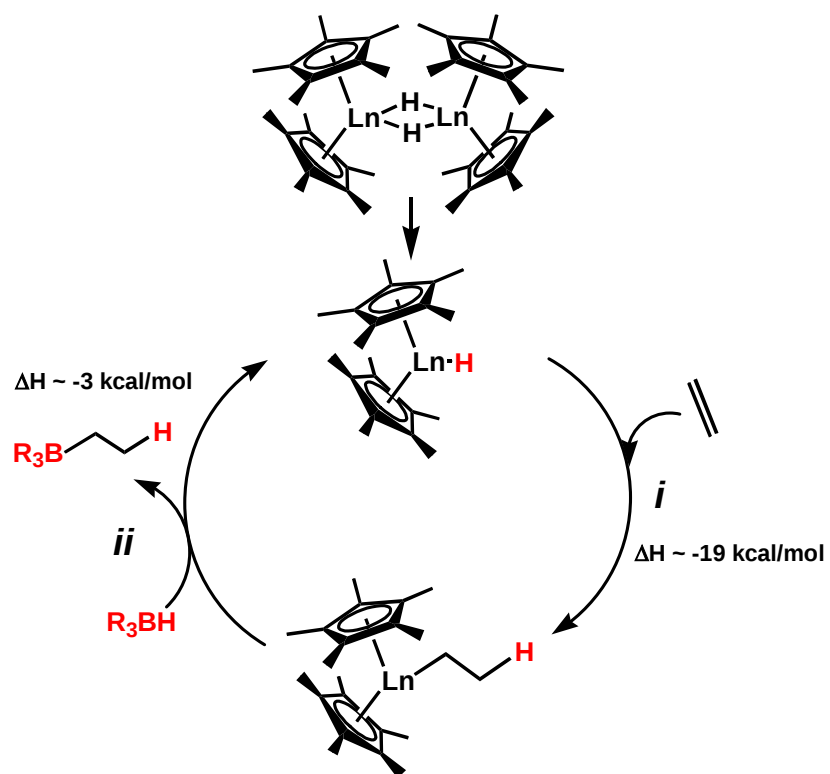


The development of electron-deficient/neutral and electron-rich chain-transfer processes was founded on key reactivity and mechanistic advances in small-molecule hydrofunctionalization. Olefin hydrosilylation processes provide the basic mechanistic sequences which allow organosilanes to function as chain-transfer agents in olefin polymerization processes (Scheme 1-4).<sup>16</sup> Here, exothermic olefin insertion into a Ln-H bond, for which there is substantial literature precedent,<sup>17</sup> is followed by a turnover-limiting and exothermic<sup>18a,b</sup> M-C/Si-H transposition<sup>19</sup> process. Mechanistic studies<sup>17d</sup> reveal that turnover frequency and selectivity for 2,1 addition regiochemistry in  $\alpha$ -olefin hydrosilylation are enhanced by a more open catalyst-ancillary ligation sphere. For styrenic olefins, a rate enhancement is observed in the presence of *para* electron-donating substituents, in addition to complete regioselective delivery of the Si moiety to the benzylic position. Furthermore, enantioselective hydrosilylation with chiral, C<sub>1</sub>-symmetric lanthanocene catalysts affords ee values as high as 68 %.<sup>17d</sup> Similarly, organolanthanide-mediated hydroboration studies<sup>20</sup> reveal catalytic pathways parallel to those defined for organolanthanide-mediated hydrosilylation (Scheme 1-5). Indeed, a wide variety of aryl- and alkyl-substituted, acyclic, and cyclic olefinic substrates can undergo efficient, catalytic hydroboration with high turnover frequencies.<sup>21c</sup>

**Scheme 1-4.** Proposed Catalytic Cycle for Organolanthanide-Mediated Olefin Hydrosilylation.

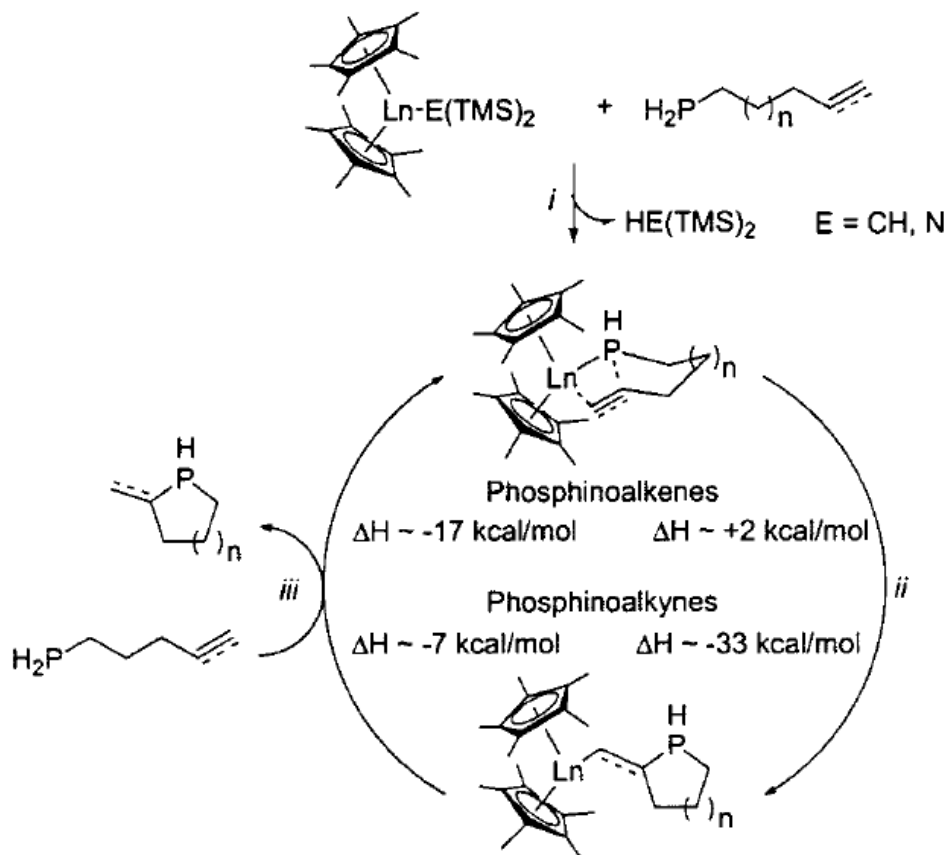


**Scheme 1-5.** Proposed Catalytic Cycle for Organolanthanide-Mediated Olefin Hydroboration.



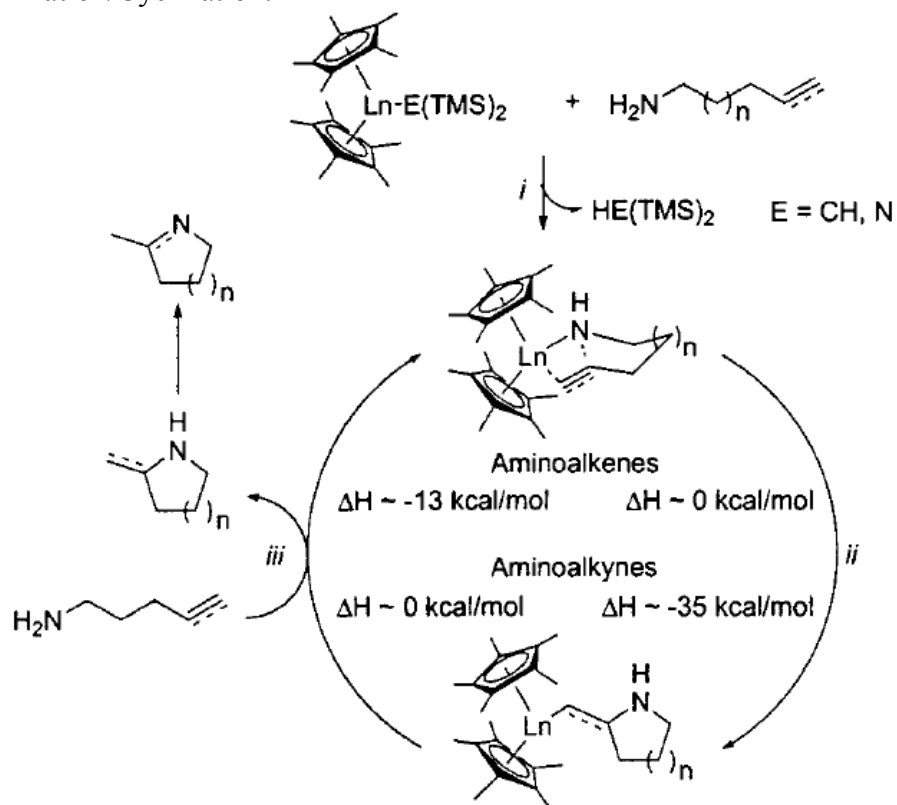
In contrast to the aforementioned hydrosilylation/hydroboration systems, small-molecule hydrophosphination and hydroamination cycles proceed via completely different pathways, in part due to the dramatically different heteroatom Lewis basicities and bond polarities of P-H/N-H versus Si-H/B-H linkages.<sup>21</sup> Mechanistic/thermodynamic analysis of organolanthanide-catalyzed hydrophosphination/cyclization pathways<sup>19c-f</sup> reveals that after initial precatalyst Ln-C protonolysis (Scheme 1-6, step i), insertion of C-C unsaturation into a Ln-P bond (Scheme 1-6, step ii) should be exothermic for alkynes and approximately thermoneutral for alkenes, followed by exothermic protonolysis of the resulting Ln-C bond (Scheme 1-6, step iii) to release the cyclized product.<sup>22</sup> Organolanthanide-mediated hydrophosphination/cyclization kinetic studies<sup>23</sup> reveal that larger metal ions and more open catalyst ancillary ligand systems lead to increased turnover frequencies for phosphinoalkynes, whereas intermediate-sized metal ions with bis(pentamethylcyclopentadienyl) ligation lead to maximum turnover frequencies for phosphinoalkenes. At high substrate conversions, heterocyclic product inhibition is sometimes observed due to competitive binding of product versus substrate. Interestingly, homoleptic lanthanide complexes (LnR<sub>3</sub>) have also proven to be effective hydrophosphination catalysts with high turnover frequencies and good selectivities. In addition, DFT/B3LYP-level theoretical analysis of these hydrofunctionalization processes<sup>23</sup> reveals that olefin insertion into the Ln-P bond via a chair-like transition state is approximately thermoneutral for alkenes, supporting the aforementioned experimental observations, and that protonolysis by incoming phosphine to regenerate the Ln-P active species is plausibly the turnover-limiting step in some cases. These theoretical studies also support the experimental observations of competitive product/unconverted substrate binding to the Ln center, which leads to product inhibition at high

**Scheme 1-6.** Proposed Catalytic Cycle for Organolanthanide-Mediated Intramolecular Hydrophosphination/Cyclization.



conversions. Together, experiment and computation define the basic details of the processes by which phosphines will be shown to function as efficient chain-transfer agents in olefin polymerizations. Detailed scope and mechanism studies of organolanthanide-mediated small molecule hydroamination<sup>24</sup> implicate processes similar, to those discussed above for hydrophosphination, and which should enable amine-based polyolefin chain transfer processes. The catalytic cycle for organolanthanide-mediated small molecule hydroamination/cyclization proceeds via sequences of: i) quantitative protonolysis of the precatalyst by amine, ii) turnover-limiting insertion of C-C unsaturation into the Ln-N bond via a chair-like transition state, and iii) rapid protonolysis of the resulting Ln-C bond by incoming substrate to release the heterocyclic product and regenerate the Ln-N active species (Scheme 1-7). Focusing on the most relevant aminoalkene hydroamination/cyclization studies, high diastereoselectivities and turnover frequencies for formation of five-, six-, and seven-membered heterocycles have been demonstrated. These processes are sensitive to the steric demands around the metal center, similar to the aforementioned hydrophosphinations, and exhibit pronounced increases in turnover frequency with larger Ln<sup>3+</sup> ionic radius (La > Sm > Lu) and more open catalyst ancillary ligation spheres. Competitive binding of product versus unconverted substrate to the Ln center sometimes results in product inhibition at high conversions. Furthermore, DFT/B3LYP-level theoretical analyses of hydroamination/cyclization<sup>25</sup> support rate-limiting alkene insertion into the Ln-N bond via a highly organized, chair-like four-center transition state, followed by exothermic Ln-C protonolysis to release the heterocyclic product. These hydrofunctionalization results provide the groundwork for extension to catalytic heteroatom chain transfer processes coupled to single-site olefin polymerization.

**Scheme 1-7.** Proposed Catalytic Cycle for Organolanthanide-Mediated Intramolecular Hydroamination/Cyclization.



In 1995, it was reported that, in the presence of olefins and silanes, homogeneous organolanthanide polymerization catalysts of the type  $(\text{Cp}'_2\text{LnH})_2$  ( $\text{Cp}' = \eta^5\text{-Me}_5\text{C}_5$ ) (**1a**, Figure 1) and  $\text{Me}_2\text{SiCp}''_2\text{LnCH}(\text{SiMe}_3)_2$  ( $\text{Cp}'' = \eta^5\text{-Me}_4\text{C}_5$ ) (**2**, Figure 1-1) where  $\text{Ln} = \text{La, Sm, Y, Lu}$  efficiently produce silane-terminated polyolefins with high polymerization productivities and tunable product molecular weights (up to  $10^5$  g polymer/(mol  $\text{Ln}\cdot\text{atm ethylene}\cdot\text{h}$ )).<sup>5f,h</sup> These initial results led to broad diversification of the applicable chain transfer agents as well as of the competent catalyst systems for polyolefin functionalization. The objective of this introduction is to survey and analyze the scope of electron-deficient/neutral and electron-rich chain transfer agents and processes which are effective in single-site-mediated olefin polymerization, focusing on research performed at both Northwestern University and in other laboratories. We begin with a summary of initial observations on organolanthanide-mediated olefin polymerization in the presence of silanes. We then show how this effort can be extended in several different directions based on the early silanolytic chain transfer results: (1) expansion of catalyst scope to early transition metal Group 4 systems, (2) exploration of silanolytic chain transfer in heterogeneous catalytic systems, (4) development of other electron-deficient/neutral chain transfer agents and processes such as those involving boranes and alanes, (5) development of complementary approaches with electron-rich phosphine chain-transfer agents. This introduction will lay the groundwork for the extension of chain-transfer processes to alkenylsilanes and amines in single-site olefin polymerization systems.

## I. Scope of Silanolytic Chain-Transfer Processes.

**1. Organolanthanide-catalyzed silanolytic chain transfer.**<sup>5f,h</sup> The anhydrous/anaerobic polymerization of olefins in the presence of silanes (pseudo-zero-excess) mediated by  $[\text{Cp}'_2\text{LnH}]_2$  (**1a**) and  $\text{Me}_2\text{SiCp}''_2\text{LnCH}(\text{SiMe}_3)_2$  (**2**) complexes proceeds efficiently and selectively as shown by NMR spectroscopy and gel-permeation chromatography (GPC) (Table 1). The  $\sim 1:1$   $-\text{CH}_3$ :  $-\text{CH}_2\text{SiH}_2$   $^{13}\text{C}$  NMR intensity ratios argue that silanes readily effect intermolecular chain termination and exclusively functionalize a single terminus per polymer chain. The concentrations of any vinyl chain end resonances in these materials are below the detection limits in both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, arguing that chain termination via  $\beta$ -hydride elimination (to metal center or to monomer)<sup>26</sup> is inconsequential. In addition, the resulting silane-capped polymers have relatively narrow, monomodal polydispersities (Table 1-1) consistent with a single-site polymerization process.<sup>13</sup> These catalytic polymerization systems are effective in the synthesis of silane-terminated polyethylenes, poly(ethylene-co-styrenes), and poly(ethylene-co-1-hexenes) using primary alkyl- and arylsilane chain-transfer reagents, and with high selectivities and activities (up to  $10^5$  g polymer/(mol Ln•atm ethylene•h)).

The proposed catalytic cycle for silane-mediated chain transfer (Scheme 1-8) is envisioned to proceed via coupled, well-precedented sequences of: (i) precatalyst dimer dissociation,<sup>18g</sup> (ii) initial  $\text{C}=\text{C}$  insertion into the  $\text{Ln-H}$  bond (**V**),<sup>18</sup> (iii) multiple chain propagating  $\text{C}=\text{C}$  insertions into the  $\text{Ln-alkyl}$  bond,<sup>18</sup> and (iv) silanolytic chain termination, presumably through a  $\sigma$ -bond metathesis-type transition state (**VI**),<sup>17,20,27</sup> to regenerate the catalytically-active organolanthanide hydride and close the cycle. As mentioned above in the hydrosilylation discussion, thermodynamic data for the steps in this cycle are consistent with the

experimental evidence for such reaction sequences.<sup>19</sup> Under steady-state conditions, the number-average degree of polymerization,  $P_n$ , is equal to the sum of all rates of propagation,  $\Sigma R_p$ , divided by the sum of the rates of competing chain-transfer pathways,  $\Sigma R_{ct}$  (eq 1-3). A kinetic analysis of the chain-transfer process (Figure 1-2), assuming constant [silane], [ethylene], and [catalyst] for any given reaction and that rapid reinitiation occurs after chain transfer, where silanolysis is the dominant chain transfer pathway, reveals that the number-average degree of polymerization  $P_n$  at ideal steady-state should obey eq 1-4. Here, the product polymer number-average molecular weight ( $M_n$ )

$$\overline{P}_n = \frac{\Sigma R_p}{\Sigma R_{ct}} \quad (1-3)$$

$$\overline{P}_n = \frac{\Sigma k_p [\text{olefin}]}{\Sigma k_{ct} [\text{chain-transfer agent}]} \quad (1-4)$$

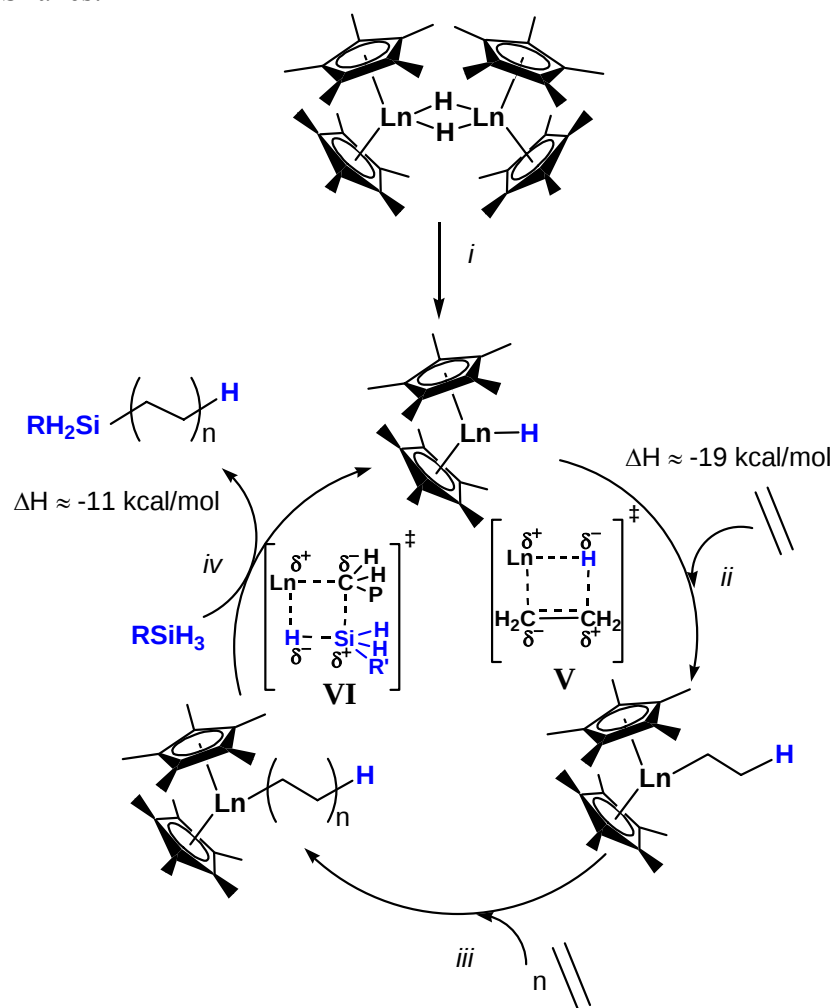
should decrease linearly with increasing [silane], typifying an ideal chain transfer process and indicating that silanolytic chain-transfer is the dominant chain termination pathway. Here  $k_p$  is the rate constant for chain propagation and  $k_{ct}$  is the rate constant for chain transfer.

**Table 1-1.** Organolanthanide-Mediated Olefin Polymerization in the Presence of Silanes.

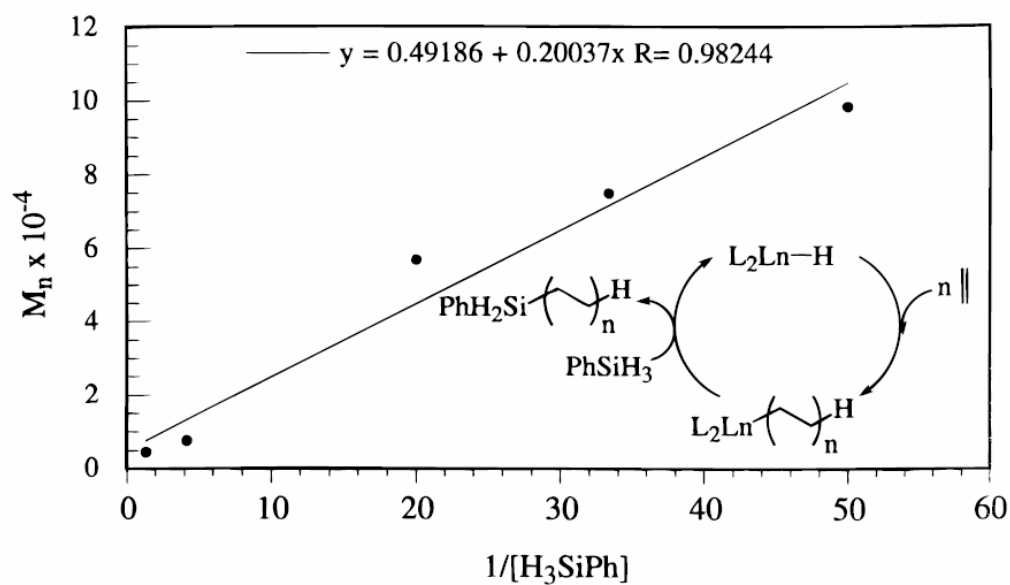
| Entry | Precatalyst <sup>a</sup>                | Silanes <sup>b</sup>                                           | Monomer <sup>c</sup> | Activity <sup>d</sup><br>( $\times 10^4$ ) | $M_n$ <sup>e</sup><br>( $\times 10^3$ ) | $M_w/M_n$ <sup>e</sup> | Yield<br>(g) |
|-------|-----------------------------------------|----------------------------------------------------------------|----------------------|--------------------------------------------|-----------------------------------------|------------------------|--------------|
| 1     | [Cp' <sub>2</sub> SmH] <sub>2</sub>     | PhSiH <sub>3</sub>                                             | E                    | 34.2                                       | 4.4                                     | 4.3                    | 0.33         |
| 2     | [Cp' <sub>2</sub> LuH] <sub>2</sub>     | PhSiH <sub>3</sub>                                             | E                    | 27.4                                       | 2.6 <sup>f</sup>                        | -                      | 0.50         |
| 3     | [Cp' <sub>2</sub> YH] <sub>2</sub>      | PhSiH <sub>3</sub>                                             | E                    | 30.0                                       | 4.9                                     | 2.2                    | 0.35         |
| 4     | [Cp' <sub>2</sub> LaH] <sub>2</sub>     | PhSiH <sub>3</sub>                                             | E                    | 82.8                                       | 4.1                                     | 3.5                    | 0.59         |
| 5     | Me <sub>2</sub> SiCp'' <sub>2</sub> SmR | PhSiH <sub>3</sub>                                             | E                    | 1.75                                       | 2.6                                     | 2.9                    | 0.24         |
| 6     | Me <sub>2</sub> SiCp'' <sub>2</sub> SmR | <i>n</i> -BuSiH <sub>3</sub>                                   | E                    | 0.636                                      | 2.1                                     | 2.4                    | 0.21         |
| 7     | Me <sub>2</sub> SiCp'' <sub>2</sub> SmR | C <sub>6</sub> F <sub>5</sub> CH <sub>2</sub> SiH <sub>3</sub> | E                    | 0.465                                      | 2.0                                     | 2.4                    | 0.23         |
| 8     | [Cp' <sub>2</sub> SmH] <sub>2</sub>     | <i>n</i> -BuSiH <sub>3</sub>                                   | E                    | 50.6                                       | 2.7                                     | 1.9                    | 0.22         |
| 9     | Me <sub>2</sub> SiCp'' <sub>2</sub> SmR | PhSiH <sub>3</sub>                                             | E/1-Hx               | 0.242                                      | 0.4                                     | 4.9                    | 0.24         |
| 10    | Me <sub>2</sub> SiCp'' <sub>2</sub> NdR | PhSiH <sub>3</sub>                                             | E/S                  | 0.257                                      | 3.3                                     | -                      | 1.70         |
| 11    | Me <sub>2</sub> SiCp'' <sub>2</sub> SmR | <i>n</i> -BuSiH <sub>3</sub>                                   | E/1-Hx               | 1.51                                       | 1.9                                     | 2.0                    | 1.00         |
| 12    | Me <sub>2</sub> SiCp'' <sub>2</sub> SmR | <i>n</i> -BuSiH <sub>3</sub>                                   | E/S                  | 0.212                                      | 1.7                                     | 2.9                    | 1.40         |

<sup>a</sup>10 - 30  $\mu$ mol precatalyst; <sup>b</sup>0.2 - 0.6 M silane; <sup>c</sup>E = ethylene, 1-Hx = 1-hexene, S = styrene; <sup>d</sup>Units = g/(mol Ln  $\cdot$  hr  $\cdot$  atm ethylene); <sup>e</sup> By GPC in 1,2,4-trichlorobenzene vs. polystyrene standards; <sup>f</sup>By <sup>1</sup>H NMR spectroscopy.

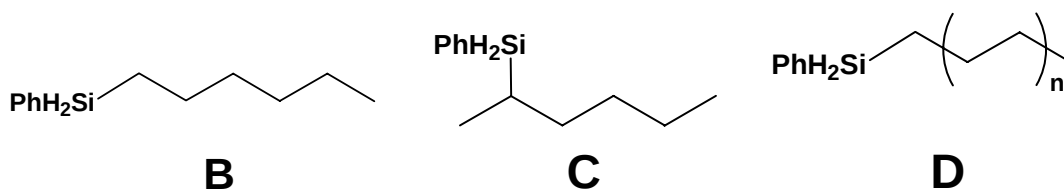
**Scheme 1-8.** Proposed Catalytic Cycle for Organolanthanide-Mediate Olefin Polymerization in the Presence of Silanes.



**Figure 1-2.** Relationship of polyethylene number average molecular weight (GPC versus polystyrene) to  $\text{PhSiH}_3$  chain transfer agent concentration for fixed organolanthanide catalyst  $[(\text{Me}_5\text{C}_5)_2\text{SmH}]_2$  and ethylene concentrations. Inset: Proposed catalytic cycle for this process.

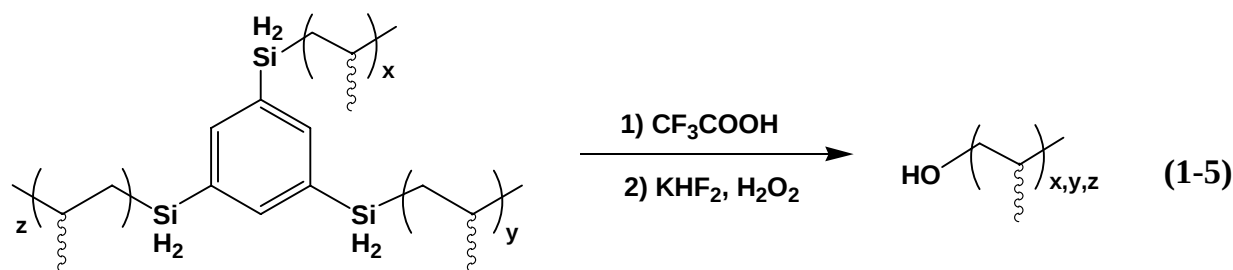


The present olefin polymerization rates in the presence of silanes are appreciably sensitive to catalyst steric encumbrances, similar to trends observed with the same catalysts for  $\alpha$ -olefin polymerizations in the absence of silanes.<sup>18g</sup> Thus, polymerization rates increase with increasing  $\text{Ln}^{3+}$  ionic radius ( $\text{La} \gg \text{Sm} \geq \text{Y} \geq \text{Lu}$ ). Interestingly, simple organolanthanide-mediated hydrosilylation of  $\text{PhSiH}_3$  with  $\alpha$ -olefins yields a mixture of 1, 2 and 2, 1 regiochemistries (e.g., **B** and **C**, respectively in the case of 1-hexene), whereas the terminus-only regiochemistry of the silane-capped polyolefin (e.g., **D**) argues that Si-C bond formation arises from direct chain transfer (Scheme 1-4, step iv) rather than from hydrosilylation of a previously formed  $\beta$ -H elimination product. As discussed in the previous section, high selectivity for 2,1 regiochemistry in olefin hydrosilylation increases with more open catalyst-ancillary ligation spheres, resulting in products such as **C**.

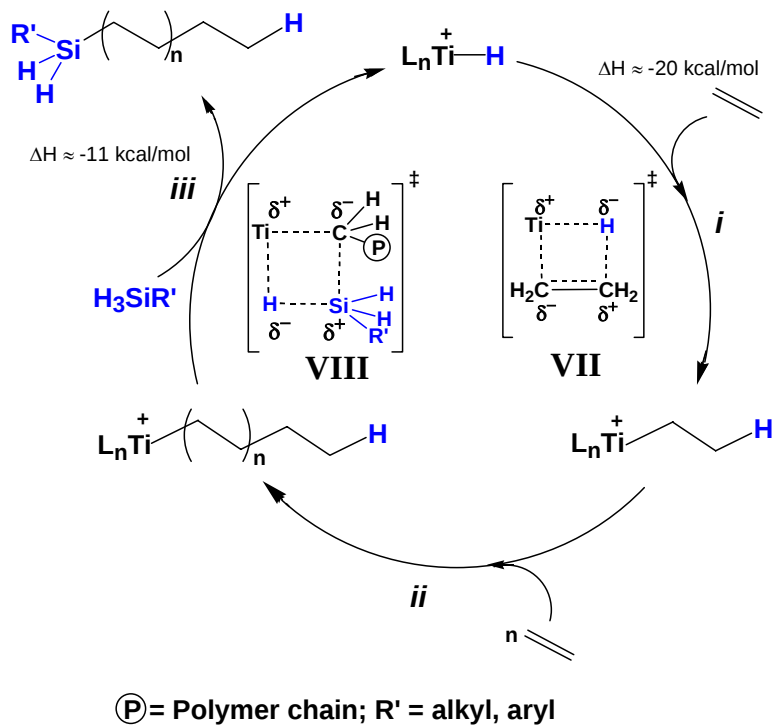


**2. Group 4-mediated alky/arylsilane chain transfer.**<sup>5e,g</sup> The success of organolanthanide-mediated silane chain transfer led us to inquire whether analogous chain transfer processes in Group 4-mediated polymerization systems are viable. Thus, organotitanium complexes **3a**, **4**, and **5** (Figure 1-1) efficiently produce a diversity of silane-terminated polyolefins, which have been characterized by GPC as well as by  $^1\text{H}/^{13}\text{C}/^{29}\text{Si}$  NMR spectroscopy. Silanolytic chain transfer doubtless proceeds via an essentially similar mechanistic scenario as in the organolanthanide-mediated polymerization systems (Scheme 1-9)

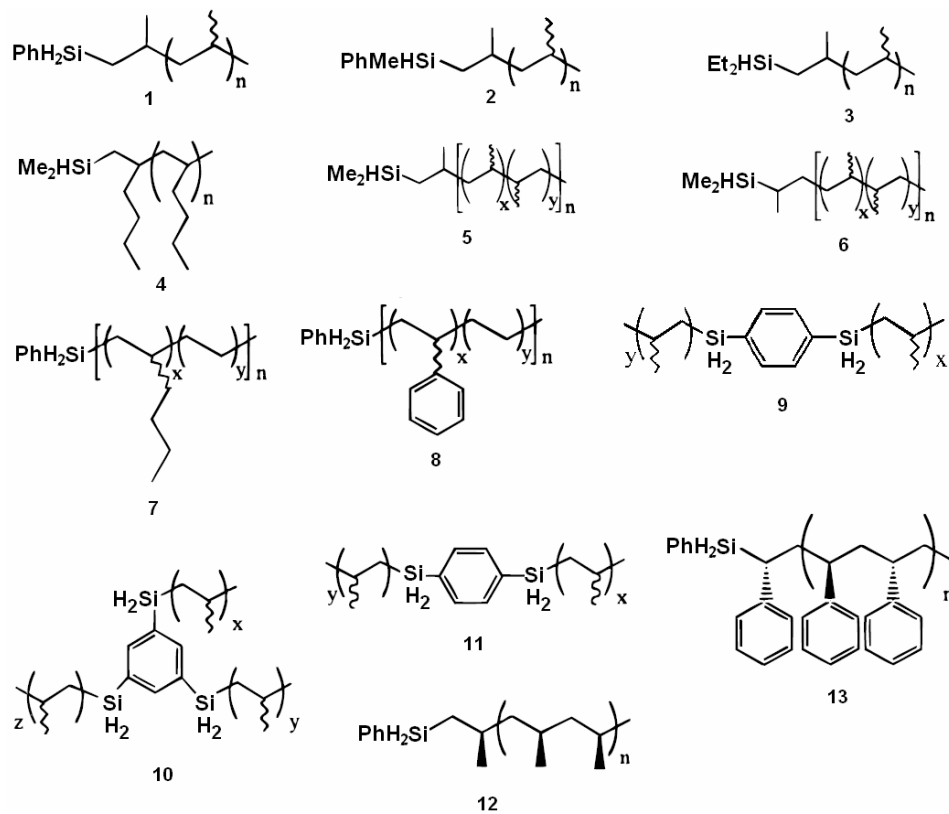
with rapid ethylene insertion/chain propagation and turnover-limiting silanolytic chain transfer (Scheme 1-9, step iii). There is extensive literature precedent for this type of M-C/Si-H four-center transposition reaction as noted in the previous section.<sup>20,28</sup> Similarly, high activities (up to  $10^6$  g polymer/(mol Ti•atm ethylene•h)) are observed for propylene, 1-hexene, ethylene/styrene, ethylene/1-hexene, propylene/1-hexene, and styrene polymerizations in the presence of silanes, with no detectable formation of  $\beta$ -H elimination-derived vinyl-terminated polymer contaminants. A wide variety of silane-capped stereoregular and random homo- and copolymers as well as block copolymers can be selectively synthesized (Figure 1-3). These silane-terminated polyolefins contain versatile, reactive C-Si functionalities that can further undergo a diverse range of subsequent and useful transformations.<sup>28</sup> One example of such a transformation is the protodesilylation and oxidative cleavage of silane-terminated atactic polypropylenes to produce hydroxy-terminated atactic polypropylenes (eq 1-5).<sup>5e</sup>



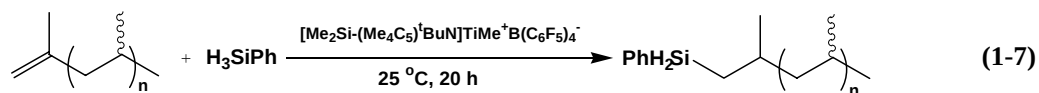
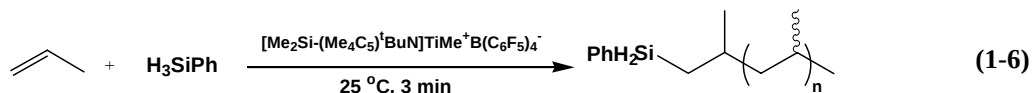
**Scheme 1-9.** Proposed Catalytic Cycle for Organotitanium-Mediated Olefin Polymerization in the Presence of Silane Chain Transfer Agents.



**Figure 1-3.** Silane-functionalized polyolefins accessible via catalytic olefin polymerization + silane chain transfer processes mediated by organotitanium catalysts.

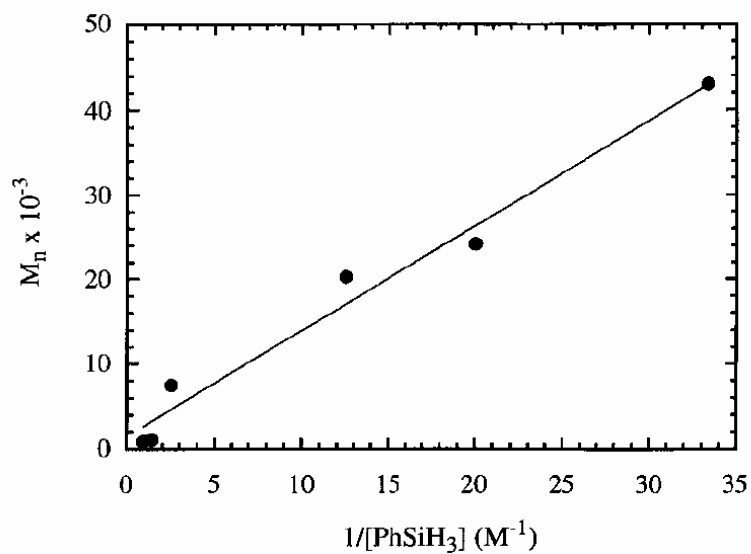


Secondary silanes used as chain-transfer agents in these organotitanium-mediated systems exhibit somewhat diminished reactivity versus primary silanes. However, as the concentration of secondary silane is increased in these systems, the yield of silane-capped polymer produced increases linearly. Note that the hydrosilylation of the analogous vinyl end group-terminated polyolefins (produced via  $\beta$ -H elimination in the absence of silane chain-transfer agents) under identical reaction conditions, yields silane-capped polymers only after 20 h of reaction time (i.e., eq 1-6 vs. eq 1-7), indicating that this pathway makes negligible contribution to the catalytic production of silane-terminated polyolefins. The chain transfer behavior of silanes in organotitanium-mediated systems is well-behaved, as supported by the

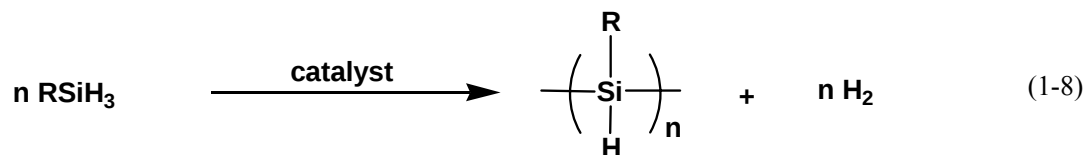


linear decrease in product polymer  $M_n$  with increasing [silane] at constant [catalyst] and [monomer] (Figure 1-4, eq 1-4). Silanolytic chain termination is clearly the dominant chain transfer pathway in these organotitanium-mediated polymerization systems. Interestingly, silane-capped polyethylenes proved to be conspicuously difficult to synthesize at 25 °C using primary and secondary alky- and arylsilanes, likely due to complex competing kinetic and steric effects, suggested by the observations that: 1) silane-capped polyethylenes are produced at -25 °C, and 2) silane-capped poly(ethylene-co-1-hexene) and silane-capped poly(ethylene-co-styrene) are produced efficiently at 25 °C. Intriguingly, organozirconium and organohafnium-mediated olefin polymerizations conducted in the presence of silanes produce polyolefins devoid of silyl end groups.

**Figure 1-4.** Relationship of polypropylene number-average molecular weight (GPC versus polystyrene) to  $\text{PhSiH}_3$  chain-transfer agent concentration in the  $[\text{Me}_2\text{Si}-(\text{Me}_4\text{C}_5)^t\text{BuN}]\text{TiMe}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -mediated capping of atactic polypropylene at constant catalyst and olefin concentrations.



**3. Supported Ziegler-Natta-Mediated Silanolytic Chain-Transfer.**<sup>5d</sup> Silanolytic chain termination using supported single-site catalysts was investigated with the goal of developing a heterogeneous catalytic approach to obtaining silane-functionalized polyolefins. Catalyst precursors  $\text{Cp}_2\text{ZrCl}_2$  (**7a**), *rac*- $[\text{CH}_2\text{CH}_2\text{-(indenyl)}_2]\text{ZrCl}_2$  (**8a**),  $\text{CGCTiMe}_2$  (**4**), and  $\text{Cp}^*\text{TiMe}_3$  (**3a**) were supported on  $\text{SiO}_2/\text{MAO}$  (calcined silica surface area  $\sim 250 \text{ m}^2/\text{g}$ , treated with MAO; MAO = methylalumoxane). The polymerization activities of these supported, single-site Group 4 catalysts in the presence of silanes are depressed to  $< 0.3 \times$  those in the absence of silanes ( $\sim 3.4 \text{ g polymer}/(\text{g catalyst} \cdot \text{atm} \cdot \text{h})$ ), and the depressed activities may be attributable to the weak Lewis basicity of the silanes. As expected, product polymer  $M_n$  also decreases upon addition of silanes to the heterogeneous polymerization systems. However, silanolytic chain-transfer in these supported systems is not particularly selective, and the resulting polyolefin products are mixtures of silane-capped and uncapped vinyl-terminated polymers or saturated polyolefins devoid of silane-capping. Using silica/MAO supported  $\text{Cp}_2\text{ZrCl}_2$  (**7a**), a mixture of  $\sim 1:1$  silane-capped: uncapped polyethylene is produced. Furthermore, the uncapped polyethylene product here contains saturated end groups, suggesting that  $\text{H}_2$  chain-transfer, likely a byproduct of well-documented organo-group 4-catalyzed dehydrogenative silane coupling (eq 1-8),<sup>29</sup> is active as a chain termination pathway.

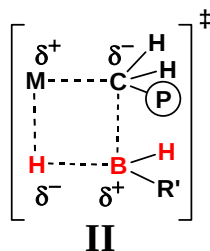


Silica/MAO-supported  $\text{CGCTiMe}_2$  (**4**) in the presence of  $\text{PhSiH}_3$  yields a 1:1 mixture of silane-capped: uncapped polyethylenes, while supported *rac*- $[\text{CH}_2\text{CH}_2\text{-(indenyl)}_2]\text{ZrCl}_2$  (**8a**) in the presence of silanes affords only product polypropylenes devoid of silane-capping and having

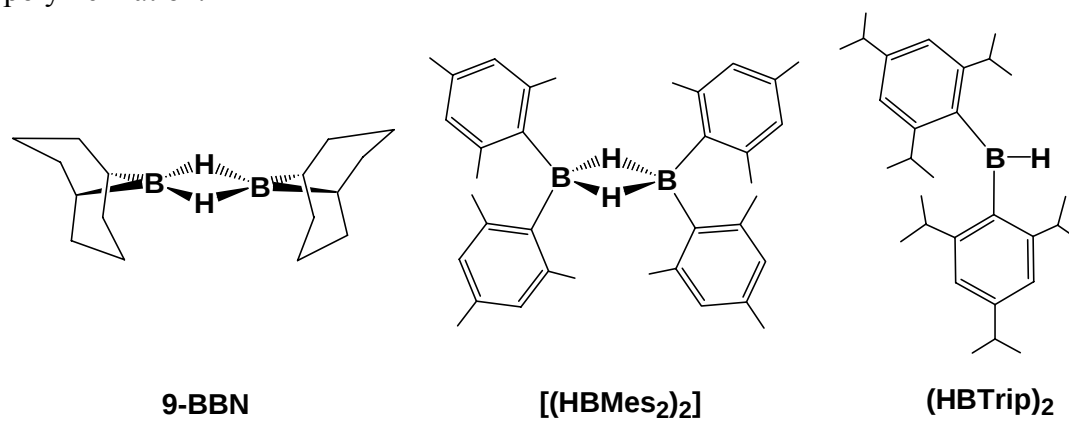
vinylidene chain ends. In addition,  $\text{SiO}_2/\text{MAO}$  supported  $\text{CGCTiMe}_2$ ,  $\text{rac}[\text{CH}_2\text{CH}_2\text{-(indenyl)}_2]\text{ZrCl}_2$ , and  $\text{Cp}^*\text{TiMe}_3$  catalyst systems in the presence of *n*-hexyl- and diethylsilane afford polyethylenes devoid of silane-capping. Thus, supported group 4 metallocenium catalysts exhibit some silanolytic chain-transfer efficiency, albeit with a narrower scope than the homogeneous systems, possibly reflecting the steric constraints imposed by the surface and ancillary ligands around the metal center.

## II. Scope of Borane Chain Transfer Processes.<sup>6</sup>

Another group of electron-deficient/neutral chain-transfer agents that have been successfully combined with single-site catalyzed olefin polymerizations are organoboranes. Thus, T.C. Chung and coworkers used 9-bora-bicyclononane (9-BBN) and other organoborane hydrides (Figure 1-5) to selectively and catalytically functionalize polyolefin chain ends. Using  $\text{Cp}^*_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$  or  $/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  to effect ethylene polymerization in the presence of 9-BBN, it was found that boranes function similarly to silanes during olefin polymerization (Scheme 1-2, transition state **II**). The turnover-limiting step in this catalytic cycle is again the  $\sigma$ -bond metathesis-type B-H/M-C transposition, resulting in the selective, efficient catalytic introduction of a boron functional group at the polyolefin terminus. This four-center<sup>28</sup> B-H/M-C

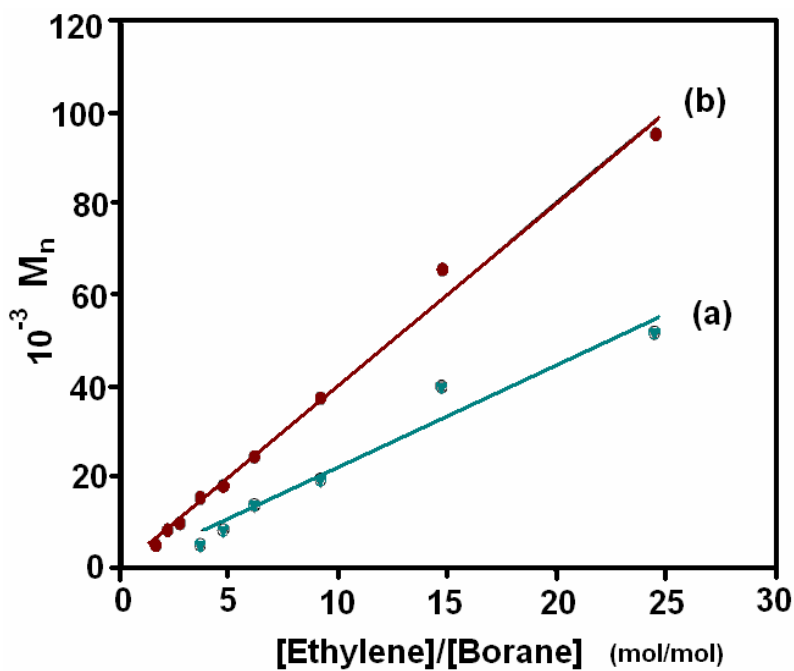


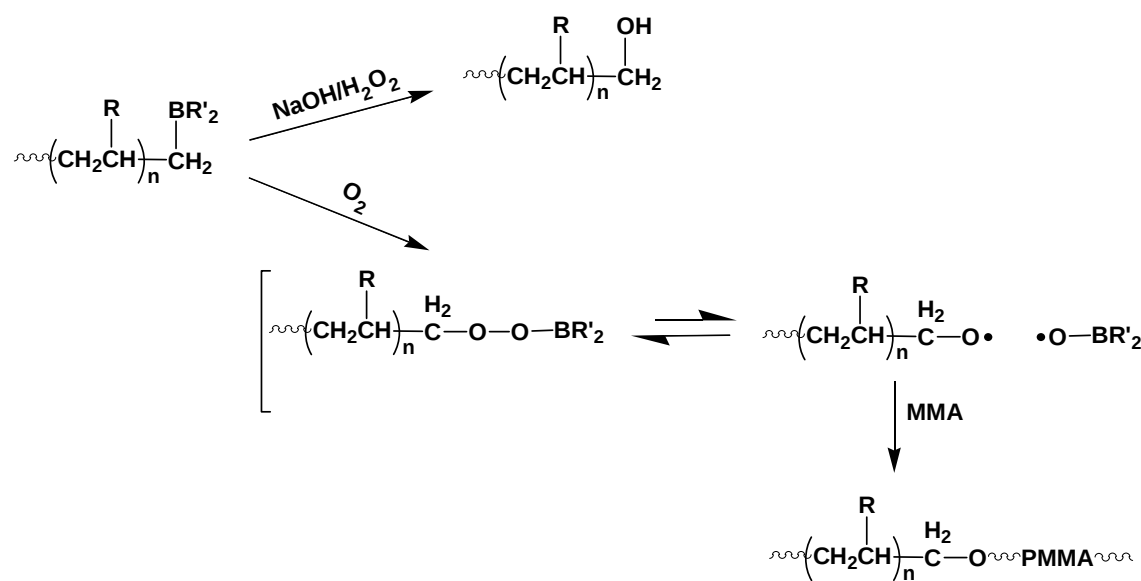
**Figure 1-5.** Borane chain-transfer agents effective in metallocene-mediated olefin polymerization.



transposition reaction has extensive literature precedent in catalytic hydroboration pathways.<sup>21</sup> In the presence of boranes, zirconocene systems **7b** and **9** (Figure 1-1) yield polyolefins with high activities (up to  $10^6$  g polymer/(mol Zr • atm • h)), and the borane chain-transfer kinetic behavior is linear and kinetically well-behaved (Figure 1-6). At constant [catalyst] and [ethylene], the product polymer  $M_n$  decreases linearly with increasing [borane], indicating that borane chain-transfer is the dominant chain termination pathway (Figure 1-6). Note that these borane-functionalized polyolefins can be subsequently oxidized to produce hydroxyl-terminated polyolefins or radical-terminated polyolefins which can then initiate a second polymerization (Scheme 1-10). Chung and coworkers next expanded this work to use CGCTiMe<sub>2</sub> (**4**) and Cp\*TiMe<sub>3</sub> (**3**) catalysts with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to produce 9-BBN-capped poly(ethylene-co-styrene), poly(ethylene-co-1-octene), and syndiotactic polystyrene.<sup>6b</sup> The scope of borane chain-transfer agents was later expanded to include dimesitylborane [(HBMeS<sub>2</sub>)<sub>2</sub>] and 2,4,6-triisopropylphenylborane (HB(Trip)<sub>2</sub>) (Figure 1-5) to selectively and efficiently produce borane-functionalized polyolefins.<sup>6b</sup>

**Figure 1-6.** Plots of number-average molecular weight ( $M_n$ ) of borane-terminated polyethylenes vs the mole ratio of: (a) [ethylene]/[9-BBN] and (b) [ethylene]/[H-B(Mes)<sub>2</sub>] in single-site mediated boranolytic chain transfer processes for ethylene polymerization. Image reproduced from reference 6b.



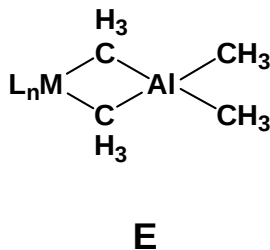
**Scheme 1-10.** Pathways for Further Functionalization of Borane-Terminated Polyolefins.

### III. Scope of Alane Chain Transfer (Chain Transfer to Aluminum)<sup>7-12</sup>

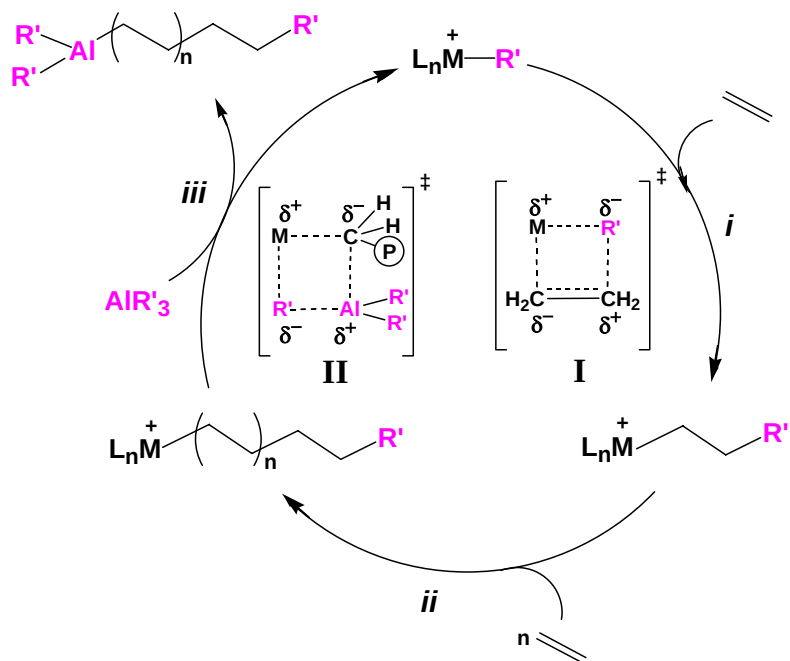
**1. Metallocene-mediated chain-transfer to aluminum.** There are numerous literature reports of olefin polymerization systems that undergo chain transfer to aluminum, referred to here as alane chain transfer.<sup>7-12</sup> For the purpose of this introduction, we limit the discussion to examples where chain transfer to aluminum is the dominant chain termination pathway. The overwhelming majority of alane chain transfer examples are reported for zirconocene-mediated propylene polymerizations in the presence of MAO or  $\text{AlR}_3$ , which exhibit activities as large as  $10^7$  g polymer/(mol Zr • atm propylene • h).<sup>8</sup> A diversity of zirconocene catalysts have been shown to mediate alane chain-transfer processes, including Cp-, indenyl-, and fluorenyl-based group 4 systems (Figure 1, complexes 7-15). The indenyl-based zirconocene catalysts, used to synthesize highly isotactic polypropylene, efficiently mediate alane chain transfer using MAO as the cocatalyst and source of alane chain-transfer agent.<sup>8b, f-h</sup> In these systems, aluminum-terminated isotactic polypropylene is selectively and catalytically synthesized as evidenced by the distinctive  $^{13}\text{C}$  NMR signal for saturated isopropyl end groups. In addition, the product polypropylene  $M_n$  decreases with increasing [MAO], indicating that alane chain transfer is the dominant chain-transfer pathway. It was also noted in some systems that alane chain transfer dominates at lower temperature, likely due to depressed, competing  $\beta$ -H elimination rates.<sup>8b</sup> Note however that other studies have argued that the residual alkylaluminum compounds ( $\text{AlR}_3$ ) typically contained in MAO samples are the species actually responsible for alane chain-transfer processes.<sup>8d,e</sup> Interestingly, these studies indicate that  $\text{AlMe}_3$  and  $\text{AlEt}_3$  both behave as efficient chain-transfer agents in zirconocene-catalyzed propylene polymerization systems, producing polymers with saturated isopropyl end groups after acidic work-up, as judged by  $^{13}\text{C}$  NMR

spectroscopy. The addition of  $\text{AlMe}_3$  and  $\text{AlEt}_3$  also results in a dramatic decrease in product polymer  $M_n$ s, again implicating alane chain transfer as the dominant chain termination pathway. In contrast, more encumbered  $\text{Al}^i\text{Bu}_3$  does not behave as an ideal chain-transfer agent, resulting in polymer molecular weights that are essentially independent of  $[\text{Al}^i\text{Bu}_3]$  as well as product polymer microstructures having negligible isopropyl end group resonances by NMR. A plausible catalytic cycle for organoaluminum chain transfer combined with single-site olefin polymerization is shown in Scheme 1-11. Note that the sigma bond metathesis transition state (II) invokes a  $\mu\text{-R}'$  moiety.

Additionally, there have also been several studies of alane chain transfer in fluorenyl- and Cp-based zirconocene-mediated propylene polymerization systems.<sup>8a,c,d</sup> These studies again indicate that addition of  $\text{AlMe}_3$  or excess MAO to the polymerization processes results in depressed product polymer  $M_n$  along with polymer microstructures containing saturated isopropyl end groups, suggesting alane chain transfer as the dominant chain termination pathway. Increasing the  $\text{AlR}_3$  or MAO concentration in the aforementioned systems generally results in decreased polymerization activity, likely due to catalyst deactivation by  $\text{AlMe}_3$ . Model compounds have been synthesized to study poisoning processes by  $\text{AlMe}_3$ , and suggest that  $\text{AlMe}_3$  substantially affects olefin polymerization due to increased  $\text{AlMe}_3$  coordinative capability (e.g., E).<sup>30</sup> Zirconocene-mediated alane chain transfer coupled to ethylene polymerization has



**Scheme 1-11.** Proposed Catalytic Cycle for Single-Site Mediated Olefin Polymerization in the Presence of Aluminum Chain-Transfer Agents.

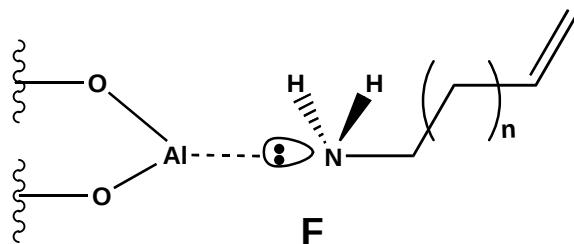


$\textcircled{P}$  = Polymer chain;  $R'$  = alkyl, aryl

also been studied,<sup>9</sup> albeit to a lesser extent compared to propylene polymerization systems. In these ethylene polymerization systems,  $\text{AlR}_3$  ( $\text{R} = \text{Me}, \text{Et}, ^i\text{Bu}$ ) compounds all behave as efficient chain-transfer agents, producing aluminum-terminated polyethylenes of molecular weights that decrease linearly with increasing  $[\text{AlR}_3]$  at constant  $[\text{catalyst}]$  and  $[\text{ethylene}]$ . Furthermore, working up the aluminum-terminated product polyethylenes with  $\text{O}_2$  or  $\text{H}_2\text{O}_2/\text{NaOH}$  affords hydroxy-terminated polyethylenes, readily identified by NMR spectroscopy and suggesting alane chain-transfer as the dominant chain functionalization/termination pathway (Scheme 1-11).<sup>9b</sup> Interestingly, metallocene-based chromium catalysts also mediate alane chain transfer in ethylene polymerization systems.<sup>9e,f</sup> Here, product polymer number-average molecular weight decreases approximately linearly with increasing  $[\text{AlR}_3]$ , suggesting alane chain transfer as the dominant chain termination pathway. Furthermore, GC-MS analyses of the product polymers indicate saturated chain ends after protonic work-up, again supporting an alane chain termination pathway.

Metallocene-mediated alane chain-transfer has also been reported in higher  $\alpha$ -olefin polymerization processes such as those involving 1-hexene,<sup>10a</sup> 1,5-hexadiene,<sup>10d,e</sup> styrene,<sup>10c</sup> and allylbenzene.<sup>10b</sup> In all of the higher  $\alpha$ -olefin polymerization systems, aluminum-terminated product polyolefins yield completely saturated end groups on protonic work-up<sup>10a-c</sup> or hydroxyl end groups after oxidative work-up.<sup>10d,e</sup> Addition of aluminum alkyls or MAO to these systems, depresses product polymer  $M_n$ , implicating alane chain-transfer as the dominant chain termination mechanism. Metallocene-mediated chain transfer to aluminum is also reported in several copolymerization systems.<sup>11</sup> Thus, zirconocene-mediated alane chain transfer occurs efficiently and selectively for ethylene/propylene copolymerizations.<sup>11a</sup>  $^{13}\text{C}$  NMR end group

analyses indicate that the majority of end groups are saturated isopropyl groups arising from chain transfer to aluminum, followed by protonic work-up. Zirconocene-mediated alane chain-transfer also proceeds efficiently in ethylene/allylbenzene copolymerization processes.<sup>11c,d</sup> Here, aluminum-terminated copolymer products are oxidatively worked-up to afford hydroxy-terminated copolymers, readily identified by NMR spectroscopy.  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses indicate complete conversion to hydroxyl end groups with no detectable vinylic  $\beta$ -H elimination products. Furthermore, product copolymer  $M_n$  decreases approximately linearly with increasing  $[\text{MAO}]$  or  $[\text{AlR}_3]$  at constant  $[\text{catalyst}]$  and  $[\text{monomer}]$ , again suggesting alane chain transfer as the kinetically dominant chain-termination pathway. Finally, zirconocene-mediated alane chain-transfer has been found to be efficient in ethylene/aminoalkene copolymerizations.<sup>11b</sup> Here, alane chain transfer is effected during the copolymerization, with activities as high as  $10^6$  g polymer/(mol Zr • atm ethylene • h). The activities are not depressed despite the presence of Lewis basic amine functional groups, likely due to binding of the amine moieties by the Lewis acidic aluminum alkyl species (e.g., **F**). NMR analyses of the product copolymers reveal saturated isopropyl end groups and the complete absence of any vinyl resonances,



suggesting that competing  $\beta$ -H elimination processes are negligible and that alane chain transfer is the dominant chain growth termination pathway. Additionally, the aluminum-terminated copolymer products can be converted to hydroxy-terminated copolymers by oxidative work-up,

indicating selective transfer of aluminum to the polymer chain termini. Product copolymer  $M_n$  decreases approximately linearly with increasing [MAO] at constant [catalyst] and [monomer], again suggesting alane chain transfer as the dominant chain termination mechanism (Scheme 1-11).

**2. Non-Metallocene-mediated chain transfer to aluminum.**<sup>12</sup> Alane chain transfer is known to be operative, not only in metallocene-catalyzed olefin polymerizations, but also in non-metallocene single-site systems, demonstrating the pronounced versatility of alane chain-transfer agents. The majority of examples of alane chain transfer mediated by non-metallocene polymerization catalysts are for ethylene polymerization processes.<sup>12a,b,d-k</sup> Here, early transition metal-based catalyst systems, including bis(phenoxyimine)-<sup>12b</sup> (**16**) and tris(pyrazolyl)borate-based<sup>12e,g,h</sup> (complexes **17-19**) catalysts undergo extremely efficient alane chain-transfer processes in conjunction with polymerization. In these examples, product polyethylene  $M_n$  decreases approximately linearly with increasing [MAO] or [AlMe<sub>3</sub>] at constant [catalyst] and [ethylene], consistent with alane chain transfer being the dominant operative chain termination pathway. In addition, <sup>1</sup>H and <sup>13</sup>C NMR analyses reveal saturated end groups and the absence of vinyl resonances, again indicating as above that  $\beta$ -H elimination processes are negligible and that alane chain transfer dominates the chain-termination pathways. Chelating diamide-based titanium complexes **20** have also been employed to successfully mediate alane chain transfer in 1-hexene polymerizations.<sup>12l</sup> Again in these systems, the product poly(1-hexene)  $M_n$  decreases linearly with increasing [MAO] at constant [catalyst] and [1-hexene], thus indicating that alane chain transfer is the dominant chain termination mechanism. <sup>1</sup>H and <sup>13</sup>C NMR analyses reveal saturated end groups, and the absence of vinylic resonances argues that  $\beta$ -H elimination

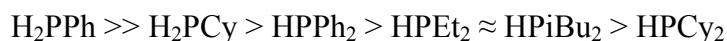
processes are negligible compared to alane chain transfer. Similar results are obtained with an organoyttrium-mediated (**21**) ethylene polymerization system in the presence of  $\text{AlR}_3$ -type alkylaluminum compounds.<sup>12a</sup>

Late transition metal catalyst (**22-24**)-mediated alane chain-transfer is also reported to be efficient when coupled to ethylene polymerization systems.<sup>12d,f,i-k</sup> These late transition metal systems produce polyethylenes with saturated end groups in the presence of aluminum alkyls ( $\text{AlR}_3$ ) or MAO with activities as high as  $10^6$  g polymer/(mol metal • atm ethylene • h). Furthermore,  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses reveal the absence of vinyl end groups, indicating that  $\beta$ -H elimination is not an important chain termination pathway here. Finally, late transition metal-mediated alane chain transfer has been reported for single-site acrylate polymerization systems, and the aforementioned criteria for efficient alane chain-transfer processes apply to these systems as well.<sup>12c</sup>

## IV. Scope of Electron-Rich Chain-Transfer Agents

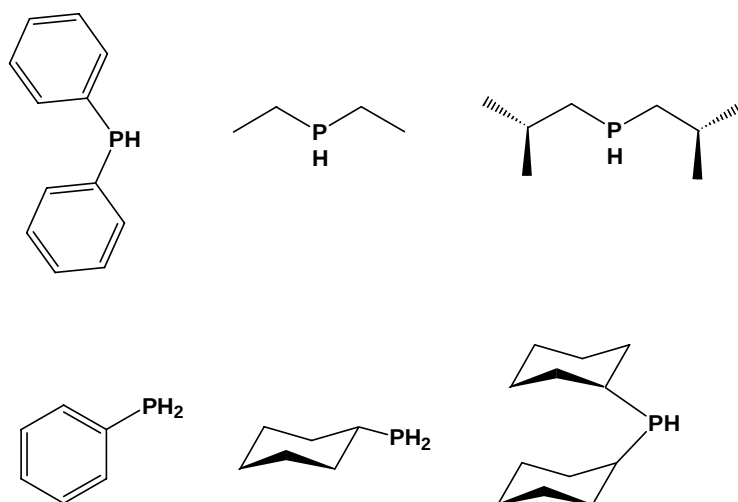
**1. Metallocene-mediated phosphine chain transfer.**<sup>15</sup> Thus far, we have discussed catalytic processes where addition of electron-deficient/neutral chain-transfer agents to single-site olefin polymerization systems results in selective and catalytic chain termination and polyolefin functionalization. The heteroatom-carbon bond-formation step involves a four-center  $\sigma$ -bond metathesis process which cleaves the metal-polymeryl linkage (Schemes 1-2, 1-4, 1-5, 1-8, 1-9, 1-11). Now we shall discuss the much less explored scope and mechanism of complementary electron-rich chain-transfer agents in metallocene-mediated olefin polymerization (Scheme 1-3). In the first example, alkyl- and aryl- as well as dialkyl- and

diarylphosphines (Figure 1-7) were used to efficiently functionalize and terminate polyethylene chains in organolanthanide catalytic systems.<sup>15</sup> In these Cp'<sub>2</sub>LnR-mediated ethylene polymerizations, activities as high as 10<sup>7</sup> g polymer/(mol Ln • atm ethylene • h) are observed in the presence of a variety of primary and secondary phosphine chain-transfer agents. The phosphine-capped product polyethylenes exhibit characteristic <sup>1</sup>H NMR resonances at δ 2.3 for –CH<sub>2</sub>PR<sub>2</sub> end groups in 1: 1 proportion to –CH<sub>3</sub> end groups. Additionally, <sup>31</sup>P NMR analysis reveals a single resonance corresponding to tertiary phosphine end groups. <sup>1</sup>H and <sup>13</sup>C NMR analyses of product functionalized polyethylenes reveal the absence of vinyl resonances, indicating that β-H elimination is not an important chain growth termination pathway here (Figure 1-8). The chain transfer efficiency trends for various phosphines parallel those of the rates of Cp'<sub>2</sub>Ln-CH(SiMe<sub>3</sub>)<sub>2</sub> (**1b**) protonolysis by the same phosphines:

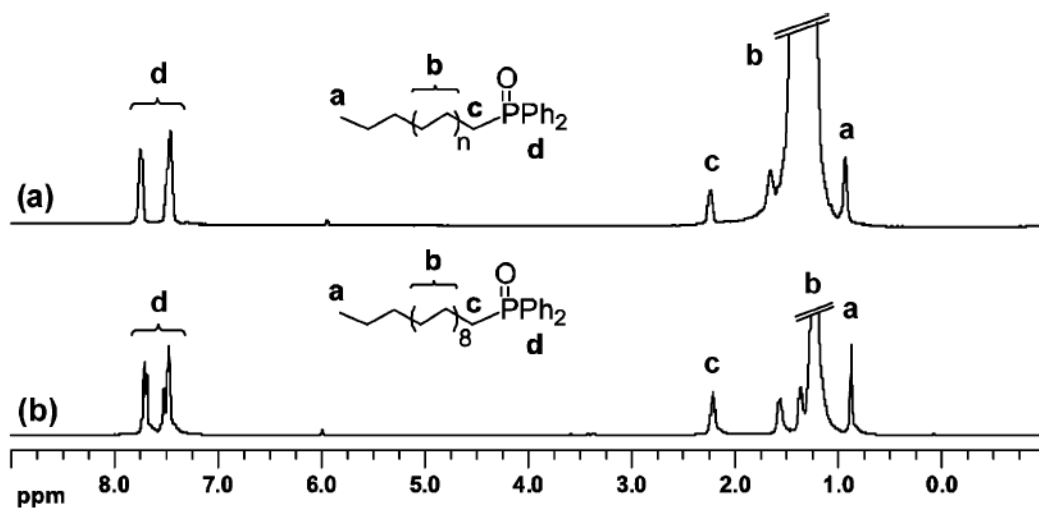


The product polyethylene  $M_n$  in these experiments decreases linearly with increasing [HPR<sub>2</sub>] at constant [catalyst] and [ethylene], indicating phosphine chain transfer to be the dominant chain transfer process in these systems (Figure 1-9). Furthermore, primary phosphines are found to be extremely efficient chain-transfer agents, producing only low molecular weight oligomers, whereas the rates of protonolyses for secondary phosphine chain-transfer agents are somewhat slower, affording higher molecular weight polyolefins under the same reaction conditions.

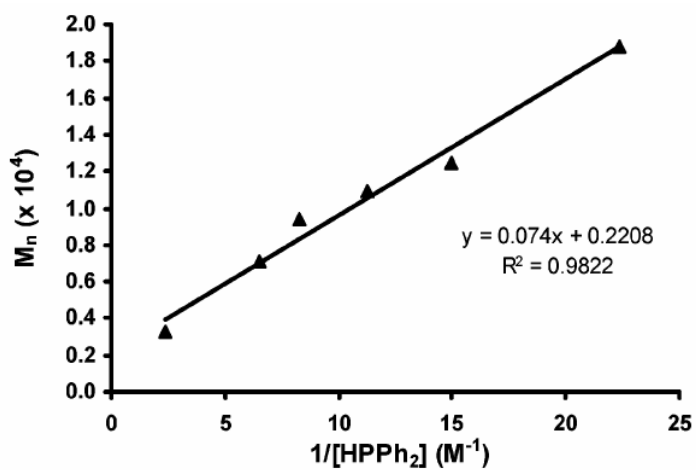
**Figure 1-7.** Phosphine chain-transfer agents used in lanthanocene-mediated olefin polymerization.



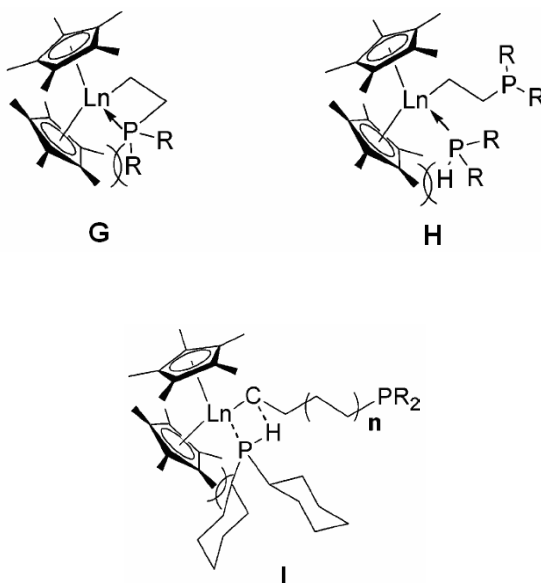
**Figure 1-8.**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) of (a) diphenylphosphine oxide-terminated polyethylene synthesized by in situ generated  $\text{Cp}'_2\text{YPPH}_2$  and (b) 1-eicosyldiphenylphosphine oxide model for the product.



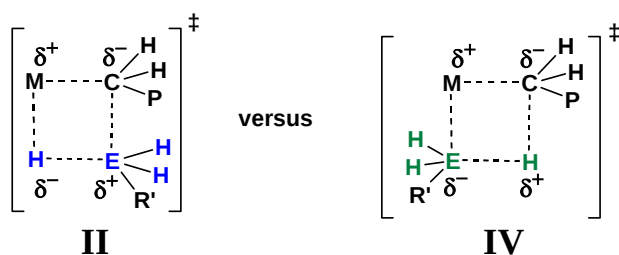
**Figure 1-9.** Relationship of diphenylphosphine-capped polyethylene number-average molecular weight (GPC vs. polyethylene standards) to inverse diphenylphosphine concentration at constant  $\text{Cp}^*\text{Ln}$ -catalyst and ethylene concentrations.



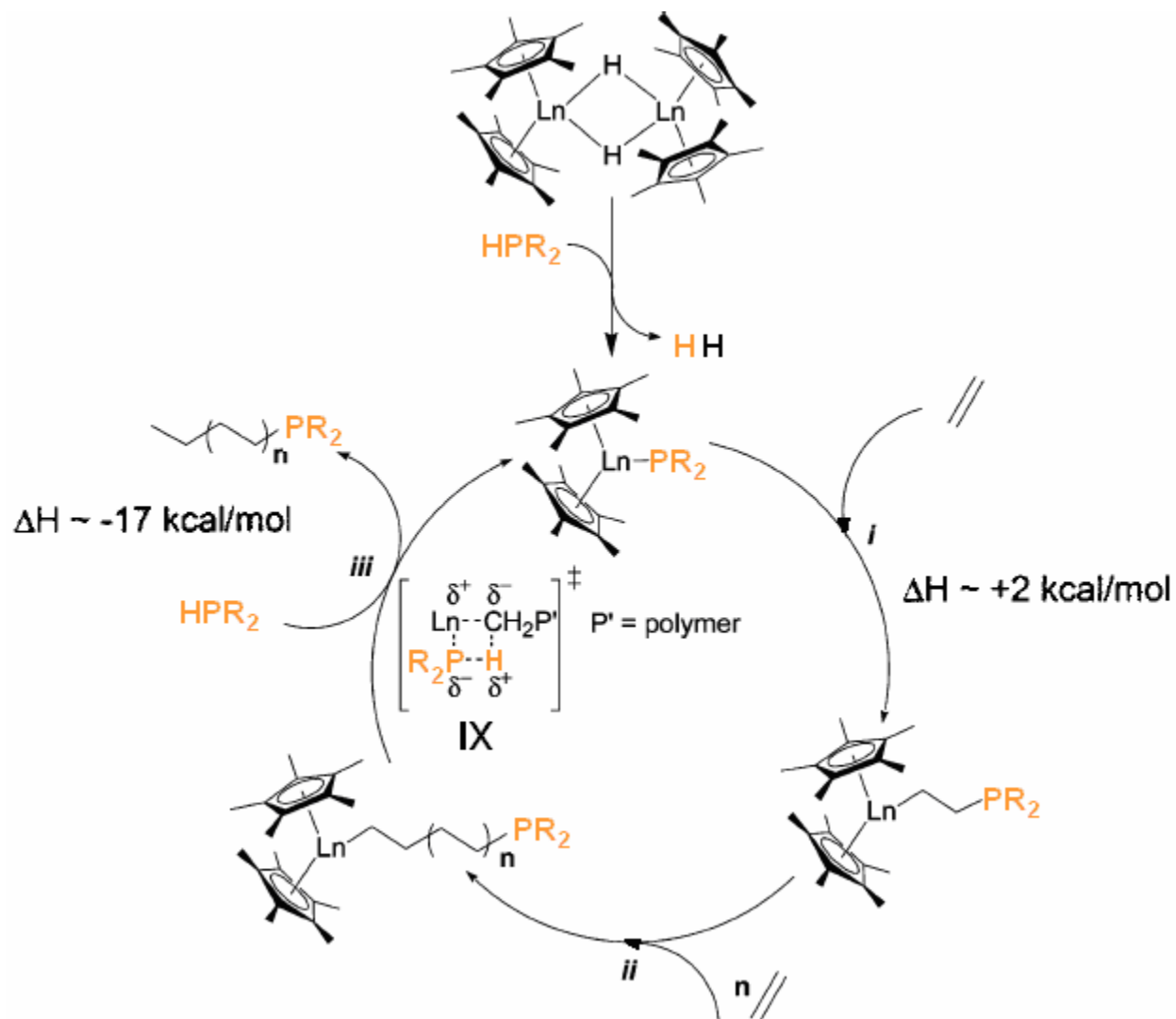
Interestingly, theoretical DFT/B3LYP-level studies of organolanthanide-mediated small molecule hydrophosphination suggest that protonolysis of the Ln-C bond by incoming phosphine substrate (step iii, Scheme 1-6) is likely turnover-limiting.<sup>24</sup> This result stands in contrast to theoretical results for hydroamination, where olefin insertion into the Ln-N bond (step iii, Scheme 1-7) is found to be turnover-limiting.<sup>26</sup> The higher molecular weight polymers produced with secondary phosphines are likely a consequence of the increased steric repulsions between the catalyst ancillary ligands and the polymeryl fragment (e.g., **G** and **H**) resulting in less favorable coordination of the phosphine to the Ln center, promoting more rapid propagation (**G**) and depressing the rate of chain-terminating protonolysis (**H**). Note here that, HPCy<sub>2</sub> (Cy = cyclohexyl) is not an efficient chain-transfer agent under these conditions for organolanthanide-mediated ethylene polymerization, presumably a consequence of severe non-bonded repulsions, as illustrated in transition state **I**. The metal ionic radius-polymerization activity trends for phosphine-capped polyethylene synthesis parallels that observed for intramolecular hydrophosphination/cyclization (Scheme 1-6), where protonolysis of the Ln-C bond by incoming



phosphine substrate is thought to be turnover-limiting:  $Y > Lu, Sm > La$ . The proposed catalytic cycle for the synthesis of phosphine-capped polyethylenes follows the sequence: i) C=C insertion into the lanthanide-phosphido bond, ii) multiple C=C insertions into the Ln-alkyl bond, iii) chain termination by protonolysis of the polymer chain and regeneration of the lanthanide-phosphido active species (Scheme 1-12). Theoretical studies on key reaction sequences support experimental evidence for the phosphine chain-transfer processes outlined above.<sup>23</sup> Note that the electronic structure of transition state **II** (Scheme 1-2) for electron-deficient chain-transfer agents is significantly different from transition state **IV** (Scheme 1-3) for electron-rich chain-transfer agents, where heteroatom delivery to carbon occurs at the beginning of the polymerization cycle.<sup>28</sup>



**Scheme 1-12.** Proposed Catalytic Cycle for Organolanthanide-Catalyzed Synthesis of Phosphine-Terminated Polyethylenes.



## V. Summary and Outlook

The outstanding efficiency of heteroatom chain-transfer agents in controlling polyolefin molecular weight while effecting *in situ* introduction of heteroatom functional groups led to the exploration of electron-deficient/neutral and electron-rich chain-transfer agents in a variety of single-site olefin polymerization systems. Alkyl- and arylsilanes are shown to be efficient in metallocene-mediated olefin homo- and copolymerization systems. These systems exhibit high polymerization activities, selectivities, and control of polymer microstructure in the presence of silanes. Metallocene-mediated olefin polymerizations in the presence of boranes are likewise shown to be extremely efficient with high productivities and selectivities, with the reactive boron groups being versatile synthons. Alane chain transfer processes span a great range of metallocene- and non-metallocene-mediated olefin polymerization systems and exhibit good efficiencies with control of polymer molecular weights. Polymer alane substituents are readily converted into other functional groups.

The mechanisms of all of these electron-deficient/neutral reagent chain-transfer processes differ substantially from those of electron-rich reagent chain-transfer processes. Despite mechanistic sequences differing in heteroatom-C bond formation at the end (electron-deficient/neutral reagents) versus at the beginning (electron-rich reagents) of the polymer-forming catalytic cycles, all of the electron-rich systems exhibit high productivities and selectivities. Phosphine chain transfer is found to be extremely efficient and selective for a variety of lanthanocene-mediated polymerization systems, introducing electron-rich chain-transfer agents into olefin polymerizations for the first time. The wide variety of elements useful in chain-transfer processes as well as the complementary use of electron-deficient/neutral and

electron-rich chain-transfer agents illustrates the diverse possibilities in this research area. Chain-transfer agent methodologies in olefin polymerization systems afford control of functionalization, reactivity, molecular weight, and microstructure of the polyolefin products. Expanding and applying this type of chain-transfer methodology to new elements and new catalytic olefin polymerization systems will be the next step in the continued effort to understand, control, and elaborate olefin polymerization processes.

## **CHAPTER 2**

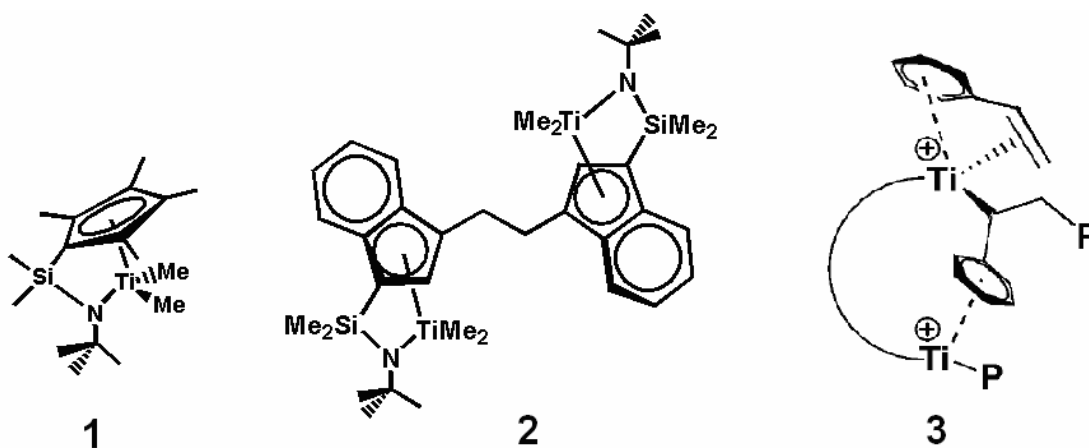
Alkenylsilane Structure Effects on Mononuclear and Binuclear Organotitanium-Mediated Ethylene Polymerization: Scope and Mechanism of Simultaneous Polyolefin Branch and Functional Group Introduction

## Introduction

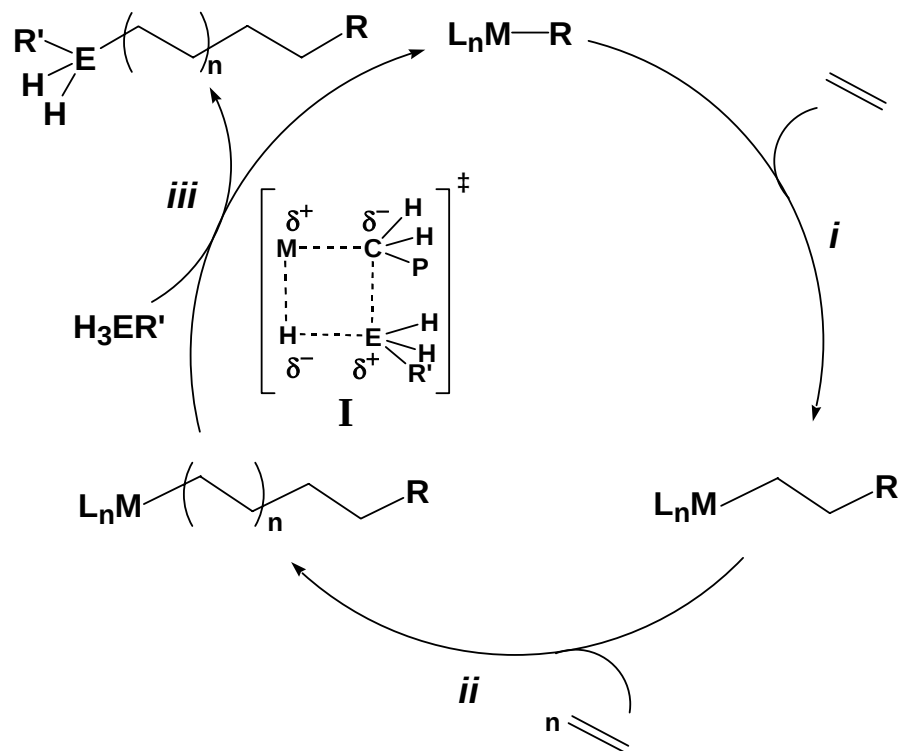
Although polyolefins have an impressive range of important applications,<sup>1</sup> their ultimate efficacy is significantly constrained by the relative chemical inertness of these macromolecules. For example, this property leads to limited adhesion and compatibility with other materials as well as less than desired processability. These deficiencies could, in principle, be overcome by controlled introduction of reactive functionality and branches into the polymer backbone. Thus, functional groups and branching offer the potential to increase polyolefin melt-fracture resistance, paintability, elasticity, compatibility with various materials, and control of shear-thinning behavior.<sup>2</sup> Despite recent advances in homogeneous olefin polymerization catalysis,<sup>1</sup> controlling polymer microstructure still remains a challenge. One approach to controlling polymer microstructure is by manipulating specific polymerization chain termination pathways. Chain transfer agents, defined as reagents which both terminate and facilitate reinitiation of a growing polymer chain, can efficiently control molecular weight and concomitantly introduce functionality at macromolecule chain ends.<sup>3, 4, 5, 6, 7, 8</sup> A priori, introducing such functionality in concert with the polymerization process is preferred over post-polymerization modification, which can be difficult due to the unreactive nature of hydrocarbon polymers and the lack of control in both macromolecule functionality levels and locations. To date, strategies to introduce comonomers that have the ability both to undergo rapid insertion (chain propagation) as well as to effect reactive functionality-introducing chain transfer processes have not to our knowledge been explored.<sup>9</sup>

Organotitanium complexes are among the most versatile catalysts for single-site Ziegler-Natta-type  $\alpha$ -olefin polymerization.<sup>10</sup> Organotitanium catalysts such as

$\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}^t\text{Bu})\text{TiMe}_2$  (CGCTiMe<sub>2</sub>, **1**), in combination with appropriate activators/co-catalysts, are known to effect the polymerization of various  $\alpha$ -olefins with activities as large as  $10^7$  g/(mol Ti • hr • atm ethylene) and to afford high molecular weight polymers with narrow polydispersities. These “CGC” catalysts produce polyethylene containing long-chain branches (LCBs) under conditions in which vinyl terminated, chain-transferred macromolecules have an elevated probability of re-enchainment into the growing polymer chain at a second catalyst center.<sup>2</sup> The resulting small but significant levels of long-chain branching, where we define a LCB as a polymeric branch, lead to extremely advantageous materials properties.<sup>2</sup> In addition, such titanium catalysts can efficiently polymerize and copolymerize sterically encumbered comonomers that have traditionally been difficult to enchain.<sup>11–12</sup> Polynuclear organotitanium catalysts, such as  $(\mu\text{-CH}_2\text{CH}_2\text{-3,3'})\{(\eta^5\text{-indenyl})[1\text{-Me}_2\text{Si}(^t\text{BuN})]\}_2\text{Ti}_2\text{Me}_4$  (EBICGCTi<sub>2</sub>Me<sub>4</sub>, **2**), also afford high molecular weight polyolefins with considerably enhanced  $\alpha$ -olefin comonomer incorporation versus mononuclear analogues.<sup>12</sup> The dicationic bimetallic framework likely exhibits greater binding affinity (e.g., **3**) resulting in enhanced comonomer enchainment.



**Scheme 2-1.** Proposed Catalytic Cycle for Organotitanium-Mediated Ethylene Polymerization in the Presence of Electron-Deficient Chain Transfer Agents

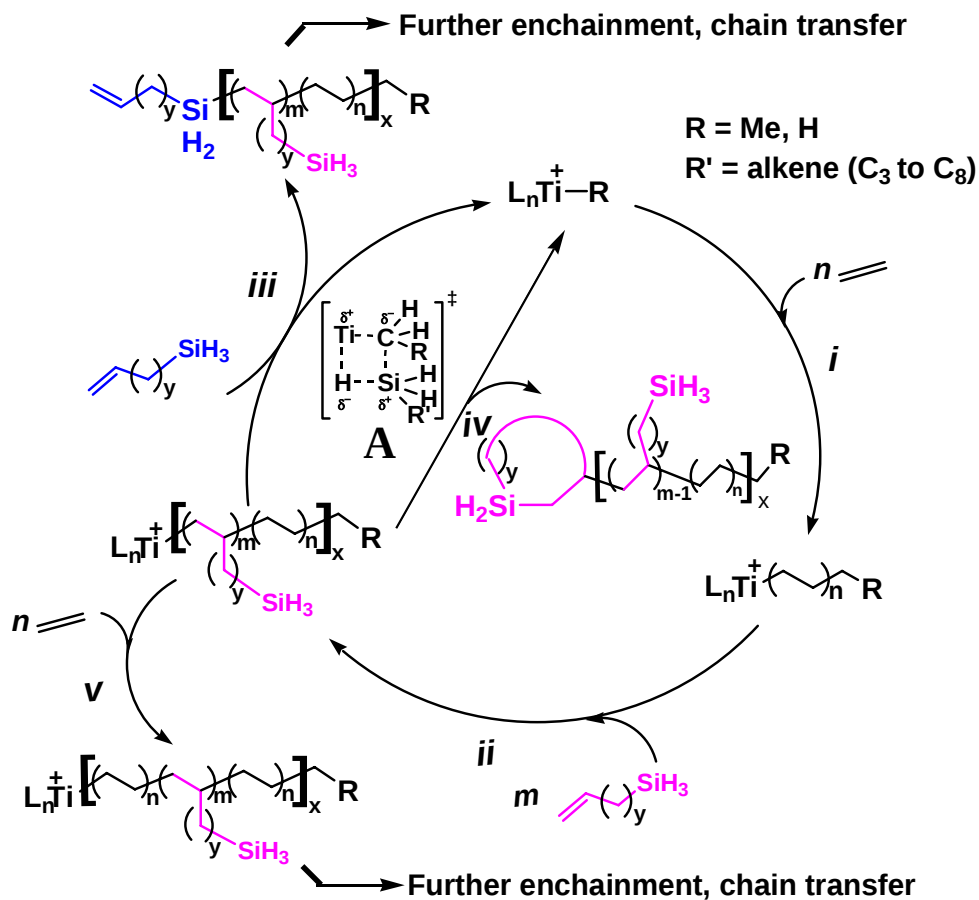


P = Polymer chain; E = Si, B, Al; R = alkyl, H; R' = alkyl, aryl

In addition to these intriguing characteristics, many single-site organotitanium catalysts exhibit high activity for silanolytic chain transfer,<sup>4b</sup> a process which efficiently introduces organosilane functionality into polyolefin chains (Scheme 2-1). These observations raise the interesting question of whether the two types of transformations could be coupled by introducing unsaturated alkenylsilanes as comonomers into a single-site olefin polymerization cycle, i.e., Scheme 2-2. For electron-deficient chain transfer agents such as alanes,<sup>3</sup> silanes,<sup>4</sup> and boranes,<sup>5</sup> the heteroatom is delivered to the polymer chain terminus at the end of each polymerization cycle as the final C-heteroatom bond-forming step (Scheme 2-1, step *iii*), and delivery is proposed to occur via four-centered  $\sigma$ -bond metathesis transition state **I**.

We previously reported<sup>4b</sup> that silane-capped polyolefins can efficiently be produced in the presence of  $\text{PhSiH}_3$  via an organotitanium-mediated catalytic cycle (Scheme 2-1;  $\text{E} = \text{Si}$ ,  $\text{R}' = \text{Ph}$ ). It was shown that polymer molecular weight can be modulated by varying the silane concentration and that the silyl group is selectively transferred to the polymer chain terminus in a process that is regiochemically distinct from that expected in a simple catalytic hydrosilylation.<sup>4</sup> Although organotitanium catalysts effectively mediate silanolytic chain transfer for many olefin polymerization processes, they are conspicuously inefficient in ethylene polymerization, for reasons not completely understood.<sup>4b</sup> Thus, silanes containing  $\alpha$ -olefinic functionality offer the intriguing potential of poisoning reactive groups in closer proximity to the Ti-C bond to afford silane-capped, branched polyethylenes, all using a single reagent/comonomer. If efficient, this process would provide an approach to simultaneously introducing both chain branching and a versatile reactive functionality<sup>13</sup> into polyolefin architectures. The proposed catalytic cycle for this synthesis of silane-capped ethylene/alkenylsilane copolymers (Scheme 2-2) is envisioned to

**Scheme 2-2.** Proposed Catalytic Cycle for Organotitanium-Mediated Alkenylsilane/Ethylene Copolymerization



proceed via sequences of: (i), (v) multiple insertions of C=C unsaturation into Ti-alkyl bonds, (ii) C=C insertion of the alkenylsilane into the growing polymer chain, and/or (iii) *intermolecular* silanolytic chain transfer to the copolymer chain, and/or (iv) *intramolecular* silanolytic chain transfer to the copolymer chain, to complete the cycle.<sup>4a</sup>

In a preliminary investigation, it was demonstrated that organotitanium-mediated ethylene/5-hexenylsilane copolymerizations yield 5-hexenylsilane-capped ethylene/5-hexenylsilane copolymers, demonstrating that coupling of insertion and chain transfer chemistry using a single comonomer is in fact an efficient process.<sup>4a</sup> We expand the scope of this exploratory study to incorporate a wider range of organotitanium catalysts of varying nuclearity as well as a series of alkenylsilane reagents of sequentially varied architecture in order to more fully investigate the scope of this organotitanium-mediated copolymer synthesis. In addition, we present a full discussion of the polymerization scope, kinetics, and mechanism involving such a dual-purpose comonomer, focusing on the effect of alkenylsilane chain length and titanium nuclearity on the course and relative efficiency of the insertion and chain transfer processes. It will be seen that by manipulating alkenylsilane chain length and Ti nuclearity, a large diversity of polyethylene architectures can be synthesized in a controlled polymerization system.

## Experimental Section

**Materials and Methods.** All manipulations of air-sensitive materials were carried out with rigorous exclusion of oxygen and moisture in flame- or oven-dried Schlenk-type glassware on a dual-manifold Schlenk line, or interfaced to a high-vacuum line ( $10^{-6}$  Torr), or in a nitrogen-filled MBraun glovebox with a high capacity recirculator ( $< 1$  ppm of  $O_2$ ). Argon and ethylene (Matheson, prepurified) were purified by passage through MnO oxygen-removal and Davison 4A molecular sieve columns. Hydrocarbon solvents (*n*-pentane and toluene) were dried using activated alumina columns according to the method described by Grubbs,<sup>14</sup> and were additionally vacuum-transferred from Na/K alloy immediately prior to vacuum line manipulations. All organic starting materials were purchased from Aldrich Chemical Co. or Strem Chemicals, Inc. and were used without further purification unless otherwise stated. Styrene and 1-hexene were stirred over  $CaH_2$  for 5 days and distilled prior to use. Allyltrichlorosilane was purchased from Acros Organics N.V. The solvent, 1,2-difluorobenzene was stirred over  $CaH_2$  for 5 days, distilled and stored over Davison 4A molecular sieves prior to use. Benzene- $d_6$ , toluene- $d_8$ , and 1,1,2,2-tetrachloroethane- $d_2$  were purchased from Cambridge Isotope Laboratories. The organotitanium precatalysts  $Me_2Si(Me_4C_5)(N^tBu)TiMe_2$ <sup>15</sup> and  $(C_5Me_5)TiMe_3$ <sup>16</sup> were prepared by published procedures. The precatalyst  $(\mu-CH_2CH_2-3,3')\{(\eta^5-indenyl)[1-Me_2Si(^tBuN)](TiMe_2)\}_2$  was prepared by the published procedure<sup>12d</sup> and activated in 1,2-difluorobenzene. The cocatalyst  $Ph_3C^+B(C_6F_5)_4^-$  was prepared by the published procedure.<sup>17</sup> The control chain transfer agent *n*-hexylsilane was synthesized from *n*-hexyltrichlorosilane according to literature procedure<sup>6</sup>, stirred over  $LiAlH_4$  for 48 h, and distilled prior to use. The comonomer allylsilane was synthesized from allyltrichlorosilane according to literature

procedure<sup>6</sup>, stirred over  $\text{LiAlH}_4$  for 48 h, and distilled prior to use. The comonomers 3-butenylsilane, 5-hexenylsilane, and 7-octenylsilane were synthesized in three steps according to modified literature procedures<sup>18, 19, 20</sup>, stirred over  $\text{LiAlH}_4$  for 48 h, and distilled prior to use.

**Physical and Analytical Measurements.** NMR spectra were recorded on either a Mercury- or Inova-400 (FT, 400 MHz,  $^1\text{H}$ ; 100 MHz,  $^{13}\text{C}$ ) or Inova-500 (FT, 500 MHz,  $^1\text{H}$ ; 125 MHz,  $^{13}\text{C}$ ) instrument. Chemical shifts ( $\delta$ ) for  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  are referenced to internal solvent resonances and reported relative to  $\text{SiMe}_4$ . For polymer NMR characterization, 50-100 mg samples were dissolved in 0.5-0.7 mL of  $\text{C}_2\text{D}_2\text{Cl}_4$  (Cambridge Isotope Laboratories) in a 5 mL NMR tube by heating the solution in a 120 °C oil bath. Melting temperatures of polymers were measured by DSC (DSC 2920, TA Instruments, Inc.) from the second scan with a heating rate of 20 °C/min. GPC analyses of polymer samples were performed on a Waters Alliance GPCV 2000 (3 columns, Waters Styragel HT 6E, HT 4, HT 2; operation temperature, 150 °C; mobile phase, 1,2,4-trichlorobenzene; flow rate, 1 mL/min) and are reported relative to 6 polyethylene standards ( $M_w$ = 560, 1214, 2155, 13600, 32100, 119600) purchased from Polymer Laboratories Inc. Light scattering experiments were conducted using the GPC-MALLS (multi-angle laser-light scattering) technique and were performed on the aforementioned Waters Alliance GPCV 2000 coupled with a Wyatt Technology DAWN EOS enhanced optical system laser photometer I55-EH (GaAs laser at 690 nm, 0.2 mm beam diameter, 85 mA operating current, and F2 glass flow cell with 64 °C heated lines). The photodetectors were calibrated with a polyethylene standard having molecular weight of 13600 g/mol and polydispersity index of 1.1 and with the elution solvent 1,2,4-trichlorobenzene. A radius of gyration value of 5 nm was assumed for this polyethylene standard. Data were analyzed by ASTRA software using a Random Coil Method.

The GPC-MALLS technique was used to determine polymer molecular weight, radius of gyration, branching ratio, and long-chain branching values.<sup>21</sup> GC-MS analyses were performed on an HP 6890 instrument equipped with a Zebron ZB-5 dimethylpolysiloxane column (30 m x 250  $\mu$ m x 0.25  $\mu$ m) interfaced to an HP 6890 mass-selective detector. Mass spectra were obtained on a VG 70-250SE (EI) or a Micromass Quattro II (ESI) high resolution mass spectrometer. Elemental analysis was performed by the Microanalysis Laboratory at the University of Illinois, Urbana-Champaign.

**Synthesis of 6-bromo-1-hexene.** A 3-neck flask, which had been dried overnight at 160 °C, equipped with a large stir bar and reflux condenser, was charged with tetraglyme (150 mL) and 1,6-dibromohexane (150 mL; Aldrich Chemical Co.) and stirred rapidly in vacuo overnight. Under a positive N<sub>2</sub> flow, the flask was then charged with 311 g (5.54 mol) pulverized KOH and 4.0 g 18-crown-6 ether (15.1 mmol) with rapid stirring. The pressure was then reduced to 100 Torr and the mixture heated at 205 °C for 1 h. The crude product, 6-bromo-1-hexene, was distilled from the reaction flask at 80 °C over the course of 30 min. The crude product was then washed with 3 x 100 mL saturated aqueous NaCl solution. The organic layer was dried over anhydrous MgSO<sub>4</sub> and filtered. The filtrate was then further distilled through a Vigreux column. Yield, 58 g (50 %). Bp 66 – 69 °C/ 40 Torr. MW 163.06 g/mol by GC-MS. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.2 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 2), 1.45 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 2), 1.75 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 2), 2.91 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 2), 4.9 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 2), 5.6 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 1).

**Synthesis of 5-hexenyltrichlorosilane.** A 3-neck flask, which had been dried overnight at 160 °C, equipped with an addition funnel, large stir bar, and reflux condenser, was attached to

a dual-manifold Schlenk line. Under a positive N<sub>2</sub> pressure, the flask was charged with 28.0 g (1.15 mol) 50-mesh Mg powder. Anhydrous diethyl ether (75 mL) and 6-bromo-1-hexene (45 mL) were next added via cannula to the addition funnel. Anhydrous diethyl ether (125 mL) and SiCl<sub>4</sub> (125 mL) were then added via cannula to the flask, and one drop of 1, 2-dibromoethane was introduced into the flask to initiate the Grignard reaction. With stirring, the substrate was added dropwise from the addition funnel over the course of 3 h and then rapidly stirred overnight. Next, the product was extracted from the resulting solids with anhydrous pentane (500 mL). After filtration, the pentane was evaporated under reduced pressure leaving ~40 mL of solution. This solution was then vacuum-transferred to a storage tube which had been dried overnight at 160 °C. The product, 5-hexenyltrichlorosilane, was purified by vacuum distillation using a Vigreux column. Yield, 36.3 g (50 %). Bp 69 – 71 °C/ 17 Torr. MW 217 g/mol by GC-MS. <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.85 (-CH<sub>2</sub>SiCl<sub>3</sub>, 2), 1.17 (-CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>, 2), 1.36 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>, 2), 1.78 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>, 2), 4.98 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>, 2), 5.65 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>, 1).

**Synthesis of 5-hexenylsilane<sup>22</sup>.** A three-necked Morton flask, which had been dried overnight at 160 °C, equipped with a large stir bar and reflux condenser, was attached to a dual-manifold Schlenk line. Under a positive N<sub>2</sub> pressure, the flask was charged with 6.00 g (158 mmol) LiAlH<sub>4</sub> and tetraglyme (75 mL). The mixture was rapidly stirred in vacuo overnight. To the stirring LiAlH<sub>4</sub> and tetraglyme mixture, 25 mL (158 mmol) hexenyltrichlorosilane was next added dropwise over the course of 1.5 h. The mixture was then stirred for an additional 3 h. The product, 5-hexenylsilane, was vacuum-transferred into a storage tube which had been dried overnight at 160 °C. Yield, 20 mL (94 %). Bp 101 – 103 °C/ 1.0 atm. MW 114 g/mol by GC-

MS.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  0.475 ( $-\text{CH}_2\text{SiH}_3$ , 2), 1.25 ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$ , 4), 1.88 ( $-\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$ , 2), 3.61 ( $-\text{SiH}_3$ , 3), 4.97 ( $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$ , 2), 5.8 ( $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$ , 1).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.32 ( $-\text{CH}_2\text{SiH}_3$ ), 26.5 ( $-\text{CH}_2\text{CH}_2\text{SiH}_3$ ), 32.4 ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$ ), 34.1 ( $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$ ), 114.7 ( $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$ ), 139.2 ( $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$ ).  $^{29}\text{Si}$  NMR (79.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -59.5.

**Synthesis of Allylsilane**<sup>23</sup>. A three-necked Morton flask, which had been dried overnight at 160 °C, equipped with a large stir bar and reflux condenser, was attached to a dual-manifold Schlenk line. Under a positive  $\text{N}_2$  pressure, the flask was charged with 14.0 g (369 mmol)  $\text{LiAlH}_4$  and tetraglyme (75 mL). The mixture was rapidly stirred in vacuo overnight. To the stirring  $\text{LiAlH}_4$  and tetraglyme mixture, allyltrimethylchlorosilane (40 mL, 276 mmol; Aldrich Chemical Co.) was added dropwise over the course of 1.5 h. The mixture was then maintained at room temperature by water bath and stirred for an additional 3 h. The product, allylsilane, was vacuum transferred into a storage tube which had been dried overnight at 160 °C. Yield, 20 mL (95 %). Bp 32 – 35 °C/ 1.0 atm. MW 72 g/mol by GC-MS.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.364 ( $-\text{CH}_2\text{SiH}_3$ , 2), 3.571 ( $-\text{SiH}_3$ ), 4.864 ( $\text{CH}_2\text{CHCH}_2\text{SiH}_3$ , 2), 5.65 ( $\text{CH}_2\text{CHCH}_2\text{SiH}_3$ , 1).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  13.657 ( $-\text{CH}_2\text{SiH}_3$ ), 114.826 ( $\text{CH}_2\text{CHCH}_2\text{SiH}_3$ ), 135.221 ( $\text{CH}_2\text{CHCH}_2\text{SiH}_3$ ).  $^{29}\text{Si}$  NMR (79.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -59.6.

**Synthesis of 3-butenyltrimethylchlorosilane.** A 3-neck flask, which had been dried overnight at 160 °C, equipped with an addition funnel, large stir bar, and reflux condenser, was attached to a dual-manifold Schlenk line. Under a positive  $\text{N}_2$  pressure, the flask was charged with 10.0 g (0.41 mol) 50-mesh Mg powder. Anhydrous diethyl ether (75 mL) and 4-bromo-1-butene (38

mL; Aldrich Chemical Co.) were then transferred via cannula to the addition funnel. Anhydrous diethyl ether (75 mL) and  $\text{SiCl}_4$  (50 mL) were then added via cannula to the flask. One drop of 1,2-dibromoethane was introduced to the flask to initiate the Grignard reaction. With stirring, the substrate was added dropwise from the addition funnel over the course of 3 h and then rapidly stirred overnight. Next, the product was extracted from the solids with anhydrous pentane (500 mL). After filtration, the pentane was evaporated under reduced pressure leaving ~40 mL of crude liquid product. This liquid was then vacuum-transferred to a storage tube which had been dried overnight at 160 °C. The product, 3-butenyltrichlorosilane, was further purified by vacuum distillation using a Vigreux column. Yield, 28.4 g (50 %). Bp 57 – 59 °C/ 45 Torr. MW 189.7 g/mol by GC-MS.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  0.93 ( $-\text{CH}_2\text{SiCl}_3$ , 2), 1.96 ( $-\text{CH}_2\text{CH}_2\text{SiCl}_3$ , 2), 4.85 ( $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{SiCl}_3$ , 2), 5.48 ( $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{SiCl}_3$ , 1).

**Synthesis of 3-butenylsilane<sup>24</sup>.** A three-necked Morton flask, which had been dried overnight at 160 °C, equipped with a large stir bar and reflux condenser, was attached to a dual-manifold Schlenk line. Under a positive  $\text{N}_2$  pressure, the flask was charged with 6.00 g (158 mmol)  $\text{LiAlH}_4$  and tetraglyme (100 mL). The mixture was rapidly stirred in vacuo overnight. To the stirring  $\text{LiAlH}_4$  and tetraglyme mixture, 22 mL (150 mmol) 3-butenyltrichlorosilane were added dropwise over the course of 1.5 h. The mixture was then stirred for an additional 3 h. The product, 3-butenylsilane, was vacuum-transferred into a storage tube which had been dried overnight at 160 °C. Yield, 11 mL (58 %). Bp 56 – 58 °C/ 1.0 atm. MW 86.2 g/mol by GC-MS.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  0.501 ( $-\text{CH}_2\text{SiH}_3$ , 2), 1.914 ( $-\text{CH}_2\text{CH}_2\text{SiH}_3$ , 2), 3.51 ( $-\text{SiH}_3$ , 3), 4.85 ( $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{SiH}_3$ , 2), 5.63 ( $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{SiH}_3$ , 1).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):

$\delta$  5.07 (-CH<sub>2</sub>SiH<sub>3</sub>), 30.3 (-CH<sub>2</sub>CH<sub>2</sub>SiH<sub>3</sub>), 139.5 (-CHCH<sub>2</sub>CH<sub>2</sub>SiH<sub>3</sub>), 114.4 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>SiH<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -59.9.

**Synthesis of 8-bromo-1-octene.** A 3-neck flask, which had been dried overnight at 160 °C, equipped with a large stir bar and reflux condenser, was charged with tetraglyme (100 mL) and 1, 8-dibromooctane (70 mL; Aldrich Chemical Co.) and stirred rapidly in vacuo overnight. Under a positive N<sub>2</sub> flow, the flask was then charged with 66.0 g (1.18 mol) pulverized KOH and 1.0 g 18-crown-6 ether (3.78 mmol) with rapid stirring. The pressure was then reduced to 50 Torr and the mixture heated at 180 °C for 4 h. The crude product, 8-bromo-1-octene, was distilled from the reaction flask at 50 °C over the course of 2 h. The crude product was then washed with 3 x 100 mL saturated, aqueous NaCl solution and 3 x 100 mL deionized water. The organic layer was next dried over anhydrous MgSO<sub>4</sub> and filtered. The filtrate was then distilled through a Vigreux column. Yield, 50 mL (78 %). Bp 90 – 93 °C/ 10 Torr. MW 191.1 g/mol by GC-MS. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.0 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 2), 1.09 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 2), 1.15 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 2), 1.45 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 2), 1.90 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 2), 2.93 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 2), 5.03 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 2), 5.73 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 1). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  28.0 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 28.3 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 28.8 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 32.8 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 33.5 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 33.9 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 114.5 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br), 138.0 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br).

**Synthesis of 7-octenyltrichlorosilane.** A 3-neck flask, which had been dried overnight at 160 °C, equipped with an addition funnel, large stir bar, and reflux condenser, was attached to a dual-manifold Schlenk line. Under a positive N<sub>2</sub> pressure, the flask was charged with 8.0 g (0.33 mol) 50-mesh Mg powder. Anhydrous diethyl ether (75 mL) and 8-bromo-1-octene (50 mL) were next added via cannula to the addition funnel. Anhydrous diethyl ether (75 mL) and SiCl<sub>4</sub> (50 mL) were then added via cannula to the flask, and one drop of 1,2-dibromoethane was introduced to the flask to initiate the Grignard reaction. With stirring, the substrate was added dropwise from the addition funnel over the course of 3 h and then rapidly stirred overnight. Next, the product was extracted from the resulting solids with anhydrous pentane (500 mL). After filtration, the pentane was evaporated under reduced pressure leaving ~40 mL of liquid product. This material was then vacuum-transferred to a storage tube which had been dried overnight at 160 °C. The product, 7-octenyltrichlorosilane, was purified by vacuum distillation using a Vigreux column. Yield, 20 mL (40 %). Bp 110 – 112 °C/ 15 Torr. MW 245.6 g/mol by GC-MS. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.91 (CH<sub>2</sub>CH(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>SiCl<sub>3</sub>, 2), 1.0 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>, 4), 1.22 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>, 2), 1.27 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>SiCl<sub>3</sub>, 2), 1.94 (CH<sub>2</sub>CHCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>SiCl<sub>3</sub>, 2), 5.01 (CH<sub>2</sub>CH(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>SiCl<sub>3</sub>, 2), 5.75 (CH<sub>2</sub>CH(CH<sub>2</sub>)<sub>5</sub>CH<sub>2</sub>SiCl<sub>3</sub>, 1). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 22.2 (-CH<sub>2</sub>SiCl<sub>3</sub>), 23.9 (-CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>), 28.5 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>), 28.8 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>), 31.6 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>), 33.9 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>), 114.5 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>), 138.8 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiCl<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ 13.2 (-SiCl<sub>3</sub>).

**Synthesis of 7-octenylsilane**<sup>25</sup>. A three-necked Morton flask, which had been dried overnight at 160 °C, equipped with a large stir bar and reflux condenser, was attached to a dual-manifold Schlenk line. Under a positive N<sub>2</sub> pressure, the flask was charged with 6.00 g (158 mmol) LiAlH<sub>4</sub> and tetraglyme (100 mL). The mixture was rapidly stirred in vacuo overnight. To the stirring LiAlH<sub>4</sub> and tetraglyme mixture, 35 mL (152 mmol) 7-octenyltrichlorosilane was next added dropwise over the course of 1.5 h. The mixture was then stirred for an additional 3 h. The product, 7-octenylsilane, was vacuum-transferred into a storage tube which had been dried overnight at 160 °C. Yield, 10 mL (86 %). Bp 162 – 164 °C/ 1.0 atm. MW 142.2 g/mol by GC-MS. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.52 (CH<sub>2</sub>CHCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>SiH<sub>3</sub>, 2), 1.12 (CH<sub>2</sub>CHCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>SiH<sub>3</sub>, 8), 1.96 (CH<sub>2</sub>CHCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>SiH<sub>3</sub>, 2), 3.64 (CH<sub>2</sub>CHCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>SiH<sub>3</sub>, 3), 5.0 (CH<sub>2</sub>CHCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>SiH<sub>3</sub>, 2), 5.8 (CH<sub>2</sub>CHCH<sub>2</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>SiH<sub>3</sub>, 1). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 5.95 (-CH<sub>2</sub>SiH<sub>3</sub>), 26.5 (-CH<sub>2</sub>CH<sub>2</sub>SiH<sub>3</sub>), 28.8 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiH<sub>3</sub>), 28.9 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiH<sub>3</sub>), 32.5 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiH<sub>3</sub>), 33.9 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiH<sub>3</sub>), 114.4 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiH<sub>3</sub>), 138.9 (CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiH<sub>3</sub>). <sup>29</sup>Si NMR (79.5 MHz, C<sub>6</sub>D<sub>6</sub>): δ -59.9 (-SiH<sub>3</sub>).

**Synthesis of *n*-hexylsilane.** A three-necked Morton flask, which had been dried overnight at 160 °C, equipped with a large stir bar and reflux condenser, was attached to a dual-manifold Schlenk line. Under a positive N<sub>2</sub> pressure, the flask was charged with 5.80 g (153 mmol) LiAlH<sub>4</sub> and tetraglyme (75 mL). The mixture was then rapidly stirred in vacuo overnight. To the stirring LiAlH<sub>4</sub> and tetraglyme mixture, 25 mL (155 mmol) *n*-hexyltrichlorosilane (Aldrich Chemical Co.) was added dropwise over the course of 1.5 h. The mixture was then

stirred for an addition 3 h. The product, *n*-hexylsilane, was vacuum-transferred into a storage tube which had been dried overnight at 160 °C. Yield, 18 mL (92 %). MW 116.17 g/mol by GC-MS.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  0.53 ( $-\text{CH}_2\text{SiH}_3$ , 2), 0.871 ( $-\text{CH}_2\text{CH}_2\text{SiH}_3$ , 2), 1.22 ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$ , 9), 3.65 ( $-\text{SiH}_3$ , 3).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  6.5 ( $-\text{CH}_2\text{SiH}_3$ ), 14.7 ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$ ), 23.3 ( $-\text{CH}_2\text{CH}_2\text{SiH}_3$ ), 27.0 ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$ ), 32.2 ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$ ), 32.9 ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$ ).  $^{29}\text{Si}$  NMR (79.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -59.6. Anal. Calcd: C, 61.98; H, 13.77. Found: C, 61.58; H, 14.01.

**Copolymerization of Ethylene and 5-Hexenylsilane. Representative Experiment.** In the glove box, a three-necked Morton flask, which had been dried overnight at 160 °C, equipped with a large stir bar and thermocouple, was charged with dry toluene (50 mL). The flask was next attached to a high vacuum line and the toluene was freeze-thaw degassed, followed by introduction of ethylene (1.0 atm) with rapid stirring. The 5-hexenylsilane (6.0 mmol) was then injected into the reactor with rapid stirring. In the glovebox, a 5.0 mL sample vial equipped with a septum cap was charged with 3.20 mg (0.010 mmol) of  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}^t\text{Bu})\text{TiMe}_2$  and 9.22 mg (0.010 mmol)  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ . A measured amount of toluene (4.0 mL) was then syringed into the vial with a dry,  $\text{N}_2$ -purged gastight syringe. The vial was shaken for several min, the contents were taken up in the syringe, and then removed from the glovebox immediately prior to the polymerization experiment. The catalyst solution was next rapidly syringed through the septum-sealed sidearm into the rapidly stirring reaction flask. After 2 min, methanol (5.0 mL) was injected to quench the reaction. Excess methanol (~ 500 mL) was then used to precipitate the polymer. The product polymer (1.5 g) was collected by filtration, washed with methanol (200 mL), and dried in vacuo at 60 °C for 48 h.  $T_m = 126$  °C.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):

$\delta$  0.25 ( $-\text{CH}_2\text{SiH}_3$ ), 0.70 ( $-\text{CH}_2\text{SiH}_2-$ ), 0.98 ( $-\text{CH}_3$ ), 1.0-1.5 ( $-\text{CH}_2-$ ), 2.2 ( $-\text{CH}-$ ), 3.6 ( $-\text{SiH}_3$ ), 3.7 ( $-\text{SiH}_2-$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  5.0 ( $-\text{CH}_2\text{SiH}_3$ ), 11.0 ( $-\text{CH}_2\text{SiH}_2-$ ), 26 ( $-\text{CH}_2\text{CH}_2\text{SiH}_3$ ), 29 ( $-\text{CH}_2-$ ), 33 ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$ ), 37 ( $-\text{CH}(\text{CH}_2)_4\text{SiH}_3$ ), 49 ( $-\text{CH}_2\text{CH}(\text{CH}_2)_4\text{SiH}_3$ ).

**Copolymerization of Ethylene and Allylsilane. Representative Experiment.** The same procedure as for the above reaction was employed, except that allylsilane (6.0 mmol) was used as the comonomer, and the polymerization was quenched after 10 sec. Yield, 1.0 g.  $T_m = 130$  °C.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  0.88 ( $-\text{CH}_2\text{SiH}_3$ ), 1.2-1.5 ( $-\text{CH}_2-$ ), 1.6 ( $-\text{CHCH}_2\text{SiH}_3$ ), 3.58 ( $-\text{SiH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  11.0 ( $-\text{CH}_2\text{SiH}_3$ ), 24 ( $-\text{CH}_2\text{SiH}_2-$ ), 26 ( $-\text{CHCH}_2\text{SiH}_3$ ), 29 ( $-\text{CH}_2-$ ), 36 ( $-\text{CH}_2\text{CHCH}_2\text{SiH}_3$ ).  $^{29}\text{Si}$  NMR (79.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -62.3 ( $-\text{SiH}_3$ ).

**Copolymerization of Ethylene and 3-Butenylsilane. Representative Experiment.** The same procedure as for the above reaction was employed, except that 3-butenylsilane (6.0 mmol) was used as the comonomer, and the polymerization was quenched after 10 sec. Yield, 0.2 g.  $T_m = 110$  °C.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  0.46 ( $-\text{CH}_2\text{SiH}_3$ ), 0.83 ( $-\text{CH}_2\text{SiH}_2-$ ), 0.98 ( $-\text{CH}_3$ ), 1.2-1.4 ( $-\text{CH}_2-$ ), 1.98 ( $-\text{CHCH}_2\text{CH}_2\text{SiH}_3$ ), 3.59 ( $-\text{SiH}_3$ ), 3.94 ( $-\text{SiH}_2-$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  5.2 ( $-\text{CH}_2\text{SiH}_3$ ), 13.2 ( $-\text{CH}_3$ ), 13.5 ( $-\text{CH}_2\text{SiH}_2-$ ), 22.2 ( $-\text{CH}_2\text{CH}_3$ ), 27.7 ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-$ ), 28.9 ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}-$ ), 29.2 ( $-\text{CH}_2-$ ), 31.5 ( $-\text{CH}_2\text{CH}_2\text{CH}_3$ ), 33.0 ( $-\text{CHCH}_2\text{CH}_2\text{SiH}_3$ ), 37.1 ( $-\text{CHCH}_2\text{CH}_2\text{SiH}_3$ ), 40.9 ( $-\text{CH}_2\text{CHCH}_2\text{CH}_2\text{SiH}_3$ ).  $^{29}\text{Si}$  NMR (79.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -24.0 ( $-\text{SiH}_2-$ ).

**Copolymerization of Ethylene and 7-Octenylsilane. Representative Experiment.** The same procedure as for the above reaction was employed, except that 7-octenylsilane (6.0 mmol) was employed as the comonomer, and the polymerization was quenched after 10 min. Yield, 0.5 g.  $T_m = 122$  °C.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  0.28 ( $-\text{CH}_2\text{SiH}_3$ ), 0.76 ( $-\text{CH}_2\text{SiH}_2-$ ), 0.84 ( $-\text{CH}_3$ ), 1.0-1.5 ( $-\text{CH}_2-$ ), 2.2 ( $-\text{CH}-$ ), 3.6 ( $-\text{SiH}_3$ ), 3.7 ( $-\text{SiH}_2-$ ).

$\text{CH}_2\text{SiH-}$ ), 0.97 ( $-\text{CH}_3$ ), 1.2-1.4 ( $-\text{CH}_2-$ ), 2.15 ( $-\text{CHCH}_2-$ ), 3.51 ( $-\text{SiH}_3$ ), 3.59 ( $-\text{SiH}_3$ ), 3.95 ( $-\text{SiH}_2-$ ), 3.99 ( $-\text{SiH}_2-$ ), 4.7 ( $-\text{SiH-}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  29.3 ( $-\text{CH}_2-$ ).

**Polymerization of Ethylene in the Presence of *n*-Hexylsilane. Representative Experiment.** In the glovebox, a three-necked Morton flask, which had been dried overnight at 160 °C, equipped with a large stir bar and thermocouple, was charged with dry toluene (50 mL). The flask was next attached to a high vacuum line and the toluene was degassed, followed by introduction of ethylene (1.0 atm) with rapid stirring. The *n*-hexylsilane (6.0 mmol) was then injected into the reactor with rapid stirring. In the glovebox, a 5.0 mL sample vial equipped with a septum cap was charged with 3.20 mg (0.010 mmol) of  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}^t\text{Bu})\text{TiMe}_2$  and 9.22 mg (0.010 mmol)  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ . A measured amount of toluene (4.0 mL) was then syringed into the vial with a dry,  $\text{N}_2$ -purged gastight syringe. The vial was shaken for several min, the contents taken up into the syringe, and then removed from the glovebox immediately prior to the polymerization experiment. The catalyst solution was next syringed through the septum-sealed sidearm into the rapidly stirring reaction flask. After 2 min, methanol (5.0 mL) was injected to quench the reaction. Excess methanol (~ 500 mL) was the used to precipitate the polymer. The product polymer (0.51 g) was collected by filtration, washed with methanol (200 mL), and dried in vacuo at 60 °C for 48 h.  $T_m = 144$  °C.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  1.2-1.4 ( $-\text{CH}_2-$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  29.3 ( $-\text{CH}_2-$ ).

**Copolymerization of Ethylene and 1-Hexene. Representative Experiment.** In the glovebox, a three-necked Morton flask, which had been dried overnight at 160 °C, equipped with a large stir bar and thermocouple, was charged with dry toluene (50 mL). The flask was next attached to a high vacuum line and the toluene was degassed, followed by introduction of

ethylene (1.0 atm) with rapid stirring. The 1-hexene (1.0 mL) was then injected into the reactor with rapid stirring. In the glovebox, a 5.0 mL sample vial equipped with a septum cap was charged with 3.20 mg (0.010 mmol) of  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}^t\text{Bu})\text{TiMe}_2$  and 9.22 mg (0.010 mmol)  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ . A measured amount of toluene (4.0 mL) was then syringed into the vial with a dry,  $\text{N}_2$ -purged gastight syringe. The vial was shaken for several min, the contents taken up into the syringe, and then removed from the glovebox immediately prior to the polymerization experiment. The catalyst solution was syringed through the septum-sealed sidearm into the rapidly stirring reaction flask. After 30 sec, methanol (5.0 mL) was injected to quench the reaction. Excess methanol (~ 500 mL) was then used to precipitate the polymer. The product polymer (1.25 g) was collected by filtration, washed with methanol (200 mL), and dried in vacuo at 60 °C for 48 h.  $T_m = 133$  °C.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  0.89 (-CH<sub>3</sub>), 1.0-1.4 (-CH<sub>2</sub>-), 1.96 (-CHCH<sub>2</sub>-), 5.4 (-CH<sub>2</sub>CH-), 5.9 (-CH<sub>2</sub>CH-).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  13.7 (-CH<sub>3</sub>), 22.6 (-CH<sub>2</sub>CH<sub>3</sub>), 26.1 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 28.3 (-CH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH-), 29.1 (-CH<sub>2</sub>-), 29.6 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH-), 32.7 (-CH<sub>2</sub>CH<sub>2</sub>CH-), 33.1 (-CH<sub>2</sub>CH-), 36.7 (-CH<sub>2</sub>CH-).

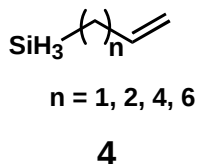
**Homopolymerization of Ethylene. Representative Experiment.** In the glovebox, a three-necked Morton flask, which had been dried overnight at 160 °C, equipped with a large stir bar and thermocouple, was charged with dry toluene (50 mL). The flask was next attached to a high vacuum line and the toluene was degassed, followed by introduction of ethylene (1.0 atm) with rapid stirring. In the glovebox, a 5.0 mL sample vial equipped with a septum cap was charged with 3.20 mg (0.010 mmol) of  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}^t\text{Bu})\text{TiMe}_2$  and 9.22 mg (0.010 mmol)  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ . A measured amount of toluene (4.0 mL) was then syringed into the vial with a dry,  $\text{N}_2$ -purged gastight syringe. The vial was shaken for several min, the contents taken up into

the syringe, and then removed from the glovebox immediately prior to the polymerization experiment. The catalyst solution was syringed through the septum-sealed sidearm into the rapidly stirring reaction flask. After 30 sec, methanol (5.0 mL) was injected to quench the reaction. Excess methanol (~ 500 mL) was then used to precipitate the polymer. The product polymer (0.60 g) was collected by filtration, washed with methanol (200 mL), and dried in vacuo at 60 °C for 48 h.  $T_m = 142$  °C.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  0.97 (-CH<sub>3</sub>), 1.0-1.4 (-CH<sub>2</sub>-).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  29.3 (-CH<sub>2</sub>-).

**Polymerizations Mediated by ( $\mu$ -CH<sub>2</sub>CH<sub>2</sub>-3,3'){( $\eta^5$ -indenyl )}[1-Me<sub>2</sub>Si (<sup>t</sup>BuN)](TiMe<sub>2</sub>)}<sub>2</sub>/ Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>. Representative Experiment.** All polymerizations were performed using the same procedures as described above, except that 3.30 mg (0.0050 mmol) ( $\mu$ -CH<sub>2</sub>CH<sub>2</sub>-3,3'){( $\eta^5$ -indenyl )}[1-Me<sub>2</sub>Si (<sup>t</sup>BuN)](TiMe<sub>2</sub>)}<sub>2</sub> and 9.22 mg (0.010 mmol) Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> were used as the catalyst and cocatalyst, respectively. In addition, polymerization reaction times for these systems are detailed Tables (2-1)–(2-6).

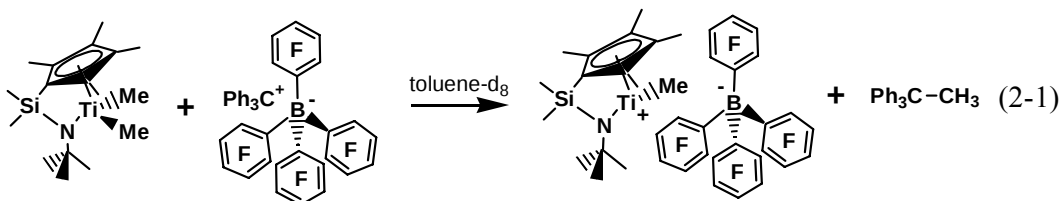
## Results

The aim of this research was to investigate the scope and mechanism of alkenylsilanes as bifunctional comonomers for organotitanium-mediated olefin polymerization. We study both mononuclear and binuclear organotitanium catalyst-mediated polymerizations (i.e., **1**, **2**) and systematically expand the comonomer scope to include  $\alpha$ ,  $\omega$ -alkenylsilanes ranging from C<sub>3</sub> to C<sub>8</sub> (**4**). After a succinct discussion of catalyst activation and M-C/Si-H transposition chemistry, we discuss the relative chain transfer efficiencies of allyl-, 3-butenyl-, 5-hexenyl-, and 7-

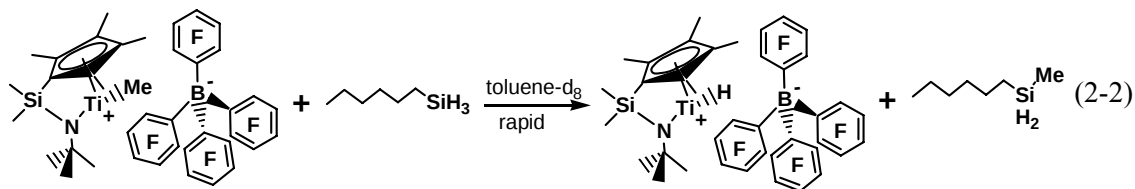


octenylsilane. Next, the effects of alkenylsilane chain length and Ti-catalyst nuclearity on polymer microstructure will be addressed from a mechanistic standpoint. Finally, mechanistic precedent in  $\alpha$ -olefin copolymerizations and silanolytic chain transfer will be employed to understand the observed trends in reactivity and polyolefin microstructure.

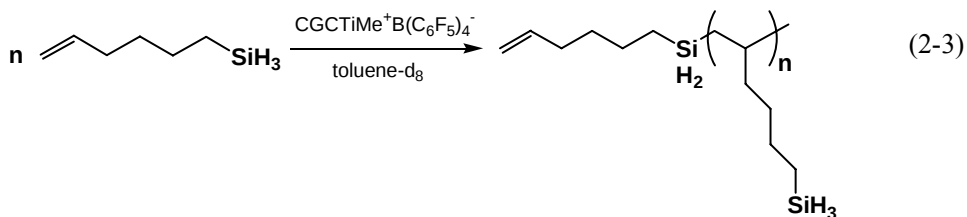
**Catalyst Activation and M-C/Si-H Transposition.** The reaction between the precatalyst CGCTiMe<sub>2</sub> and the cocatalyst Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>−</sup> produces the catalytically-active ion paired species CGCTiMe<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>−</sup> (eq 2-1).<sup>26</sup> The catalyst CGCTiMe<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>−</sup> has a relatively open



coordination sphere due to the “constrained geometry” ancillary ligand system. Similar to a variety of other organoborane/organoborate cocatalysts,<sup>1d, 27</sup> the weakly coordinating B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>−</sup> anion<sup>1d, 15a, 28</sup> plays an essential role in enhancing the olefin polymerization activity, affording productivities as high as 10<sup>7</sup> g/(mol Ti x atm ethylene x h) at 25 °C when paired with CGCTiMe<sub>2</sub>. Preliminary screens for stoichiometric M-C/Si-H transposition activity were performed by contacting CGCTiMe<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>−</sup> with C<sub>6</sub>H<sub>13</sub>SiH<sub>3</sub> in toluene-*d*<sub>8</sub>. As monitored *in situ* by <sup>1</sup>H NMR spectroscopy, rapid Ti-C/Si-H transposition occurs at room temperature, yielding (C<sub>6</sub>H<sub>13</sub>)(Me)SiH<sub>2</sub> and what is presumably a cationic organotitanium hydride (eq 2-2).<sup>1c,29</sup>



These observations next motivated additional investigations into the reactivity of 5-hexenyldimethylsilane with respect to rapid, repetitive insertion (propagation) at a single-site olefin polymerization center. Preliminary test polymerizations of  $\text{C}_6\text{H}_{11}\text{SiH}_3$  catalyzed by  $\text{CGCTiMe}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  were carried out in toluene- $d_8$ . As monitored in situ by  $^1\text{H}$  NMR spectroscopy, rapid insertion of 5-hexenyldimethylsilane into the Ti-alkyl bond occurs to produce oligomeric materials containing  $n = 5$  to  $n = 9$  monomer units based on EI mass spectrometry (eq 2-3).  $^{13}\text{C}$  NMR resonances of the oligomers indicate butyl branches, each terminated with a single silyl group, by comparison to literature data for 1-hexene homopolymers.<sup>30</sup> The  $^1\text{H}$  NMR spectrum exhibits resonances at  $\delta$  3.7 and  $\delta$  3.9 ppm, which are consistent with the presence of  $\text{SiH}_3$  and  $\text{SiH}_2$  groups, respectively.<sup>4</sup>



All of these preliminary observations motivated the detailed investigation of alkenyldimethylsilane effects on single-site, organotitanium-catalyzed olefin polymerization discussed below.

**Chain Transfer Efficiency of 5-Hexenyldimethylsilane in Organotitanium-Mediated Ethylene Copolymerizations. Polymeric Products, Nuclearity Effects, and Comparison to *n*-Hexenyldimethylsilane.** The first alkenyldimethylsilane investigated as a chain transfer agent/comonomer for

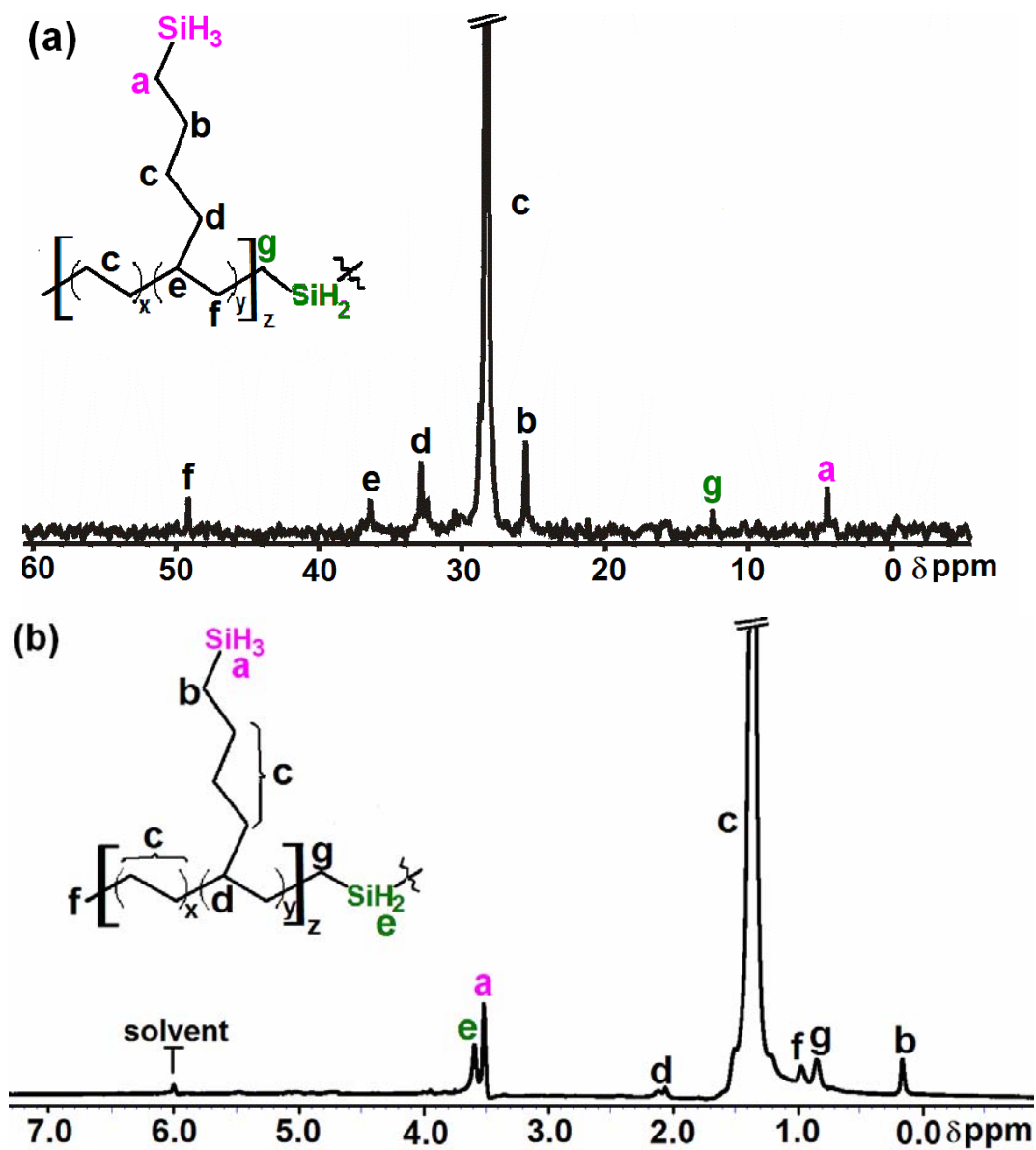
organotitanium-mediated ethylene polymerization was 5-hexenylsilane (Table 2-1). All polymerizations were performed under 1.0 atm ethylene pressure and rigorously anaerobic/anhydrous conditions using procedures minimizing mass transport effects,<sup>31</sup> with the olefin concentration held constant and the 5-hexenylsilane concentration maintained in pseudo-zero-order excess. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the silane-terminated ethylene/5-hexenylsilane copolymers exhibit characteristic proton butylsilane branch ( $\delta$  0.25, 0.70, 2.2, 3.6), polyethylene backbone ( $\delta$  1.0-1.5), and  $-\text{CH}_3$  chain end ( $\delta$  0.98) resonances (Figure 2-1).<sup>4, 7, 18</sup> In addition, the  $^{13}\text{C}$  NMR and GPC-MALLS data indicate approximately 40 butylsilane branches per 1000 carbons. The concentrations of any vinyl chain end resonances in these materials are below the detection limits in both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, suggesting that chain termination via  $\beta$ -hydride elimination (to metal center or monomer)<sup>32</sup> is inconsequential. Furthermore, the  $\sim 3:1$   $-\text{CH}_2\text{SiH}_3$ :  $-\text{CH}_2\text{SiH}_2$   $^{13}\text{C}$  NMR intensity ratio suggests that 5-hexenylsilane readily undergoes insertion into the polymer chain as well as silanolytically effects inter- and/or intramolecular chain termination and thereby functionalizes the polymer chain end. The  $-\text{CH}_2-$  resonances from cyclized end groups directly overlap with the main  $-\text{CH}_2-$  polymer backbone resonance, thus the amount of cyclized end groups cannot be quantified.

**Table 2-1.** Organotitanium—Catalyzed Ethylene Polymerization in the Presence of 5-Hexenylsilane

| Entry | Precatalyst <sup>a, b</sup>           | [Precat.] (μM) | [C <sub>6</sub> H <sub>11</sub> SiH <sub>3</sub> ] (mM) | Activity <sup>c</sup> (x10 <sup>4</sup> ) | M <sub>n</sub> <sup>d</sup> | M <sub>w</sub> / M <sub>n</sub> <sup>d</sup> | T (°C) | T <sub>m</sub> (°C) | comonomer incorporation % <sup>e</sup> |
|-------|---------------------------------------|----------------|---------------------------------------------------------|-------------------------------------------|-----------------------------|----------------------------------------------|--------|---------------------|----------------------------------------|
| 1     | Cp*TiMe <sub>3</sub>                  | 200            | 102                                                     | 7.10                                      | 4600                        | 2.4                                          | 23     | 112                 | 6.0                                    |
| 2     | CGCTiMe <sub>2</sub>                  | 200            | 12.8                                                    | 500                                       | 78600                       | 2.4                                          | 26     | 126                 | 1.0                                    |
| 3     | CGCTiMe <sub>2</sub>                  | 200            | 25.5                                                    | 290                                       | 43900                       | 2.6                                          | 24     | 125                 | 1.0                                    |
| 4     | CGCTiMe <sub>2</sub>                  | 200            | 51.1                                                    | 4.70                                      | 21100                       | 3.7                                          | 29     | 126                 | 2.0                                    |
| 5     | CGCTiMe <sub>2</sub>                  | 200            | 76.5                                                    | 0.09                                      | 15900                       | 3.3                                          | 22     | 126                 | 3.0                                    |
| 6     | CGCTiMe <sub>2</sub>                  | 200            | 102                                                     | 0.06                                      | 12700                       | 2.6                                          | 23     | 124                 | 3.0                                    |
| 7     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 12.8                                                    | 180                                       | 9600                        | 2.4                                          | 30     | 105                 | 1.0                                    |
| 8     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 19.0                                                    | 6.00                                      | 12100                       | 2.2                                          | 25     | 103                 | 1.0                                    |
| 9     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 25.5                                                    | 1.31                                      | 12500                       | 2.3                                          | 24     | 103                 | 2.0                                    |
| 10    | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 31.6                                                    | 1.43                                      | 15000                       | 2.4                                          | 25     | 106                 | 2.0                                    |
| 11    | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 51.1                                                    | 0.11                                      | 22500                       | 1.7                                          | 25     | 105                 | 2.0                                    |

<sup>a</sup>CGC = Me<sub>2</sub>Si(Me<sub>4</sub>C<sub>5</sub>)(N<sup>t</sup>Bu), EBI = Ethylene-bridged bis(indenyl); polymerization conditions: 50 mL toluene, 2.0 min. for entries 1-6, 10 min. for entries 7-11 <sup>b</sup> cocatalyst = 10 μmol Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> <sup>c</sup>Units = g/(mol Ti • hr • atm ethylene <sup>d</sup>By GPC in 1,2,4-trichlorobenzene vs. polyethylene standards <sup>e</sup> comonomer incorporation calculated based on <sup>13</sup>C NMR spectra.

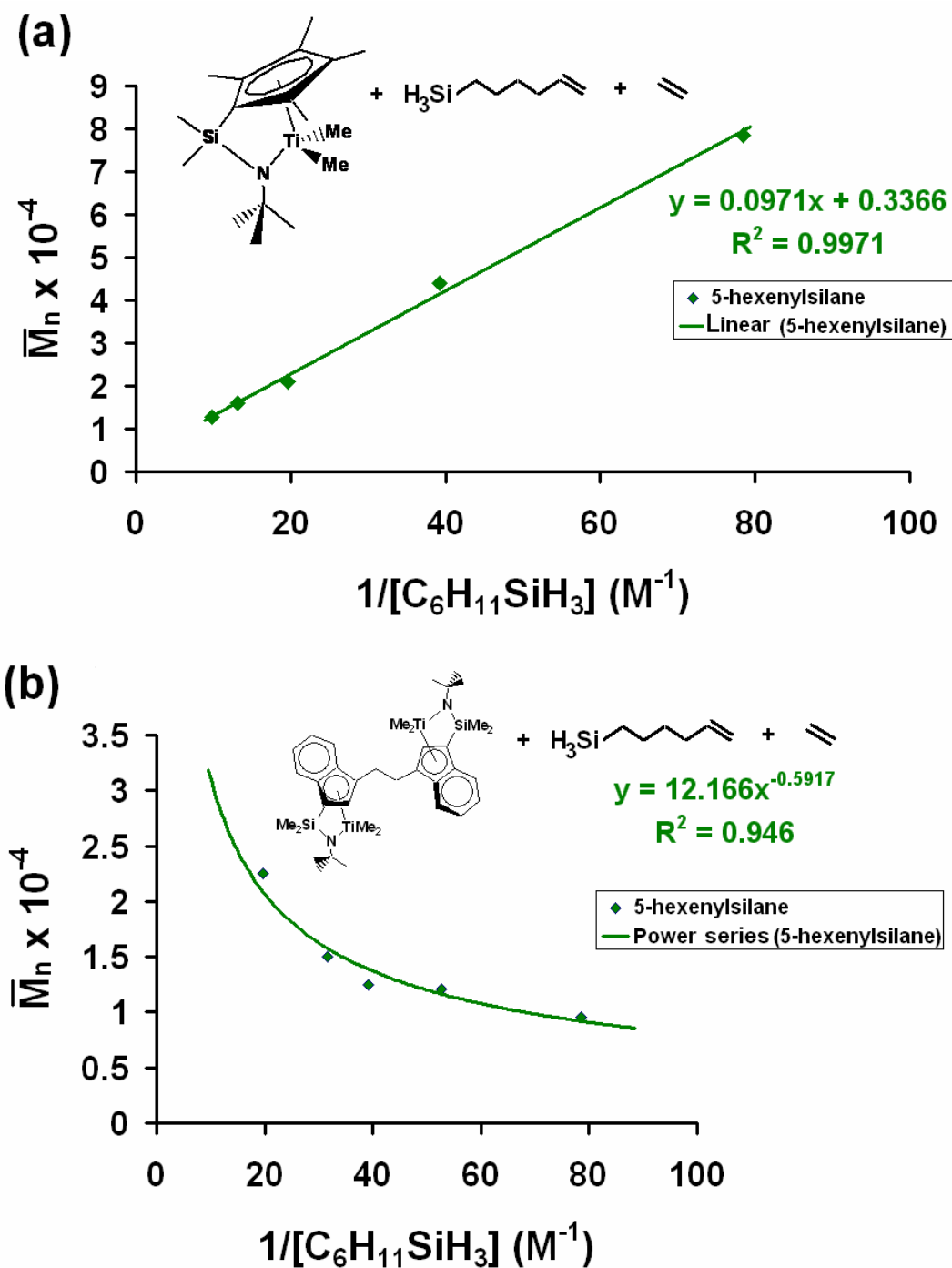
**Figure 2-1.** (a)  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum and (b)  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum of the ethylene/5-hexenylsilane copolymer produced by  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ . Assignments follow from manuscript refs. 4, 7, 18.



The  $\text{--SiH}_2\text{--}$  resonances in both the  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectra for cyclic vs. acyclic end groups cannot be distinguished from one another as seen by NMR spectroscopy on small molecule analogs (all of the  $^1\text{H}$  NMR resonances are  $\sim 4.0$  ppm and  $^{29}\text{Si}$  NMR resonances are at  $\sim -24$  ppm). In addition, the resulting 5-hexenylsilane-capped copolymers have relatively narrow, monomodal polydispersities (Table 2-1) consistent with a single-site process.

For polymerizations conducted in the presence of 5-hexenylsilane, titanium nuclearity and polymer molecular weight are inversely related. Thus, ethylene/5-hexenylsilane polymerizations catalyzed by binuclear  $\text{EBICGCTi}_2\text{Me}_4/2\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  require long reaction times (as compared to mononuclear organotitanium catalysts) to produce significant amounts of polymer having lower molecular weight ( $M_n = 12500$ ; Table 2-1, entry 9). In contrast,  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -mediated polymerizations result in copolymers with higher molecular weight ( $M_n = 43900$ ; Table 2-1, entry 3) produced with significantly higher activities ( $10^6$  g polymer/(mol Ti  $\cdot$  atm ethylene  $\cdot$  h)). The  $\text{EBICGCTi}_2\text{Me}_4/2\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  active catalyst is deep reddish-brown and maintains this color throughout the polymerization, suggesting the presence of a stable active species.<sup>12c</sup> The  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  active catalyst is bright orange and maintains this color throughout the polymerization, again suggesting the presence of a stable active species.<sup>15j</sup> In addition, at constant catalyst and ethylene concentrations, product copolymer molecular weight scales inversely with silane concentration for  $\text{CGCTiMe}_2$  (Table 2-1, entries 2-6; Figure 2-2a), supporting the chain transfer mechanism shown in Scheme 2-2 (eq 2-7, *vide infra*).

**Figure 2-2.** Relationship of ethylene + 5-hexenylsilane copolymer number-average molecular weight (GPC vs. polyethylene standards) to inverse 5-hexenylsilane concentration at fixed ethylene and (a) CGCTiMe<sub>2</sub> (b) EBICGCTi<sub>2</sub>Me<sub>4</sub> concentrations.



Interestingly, under similar conditions, product copolymer molecular weight *increases* as an approximate superlinear series with increasing silane concentration for EBICGCTi<sub>2</sub>Me<sub>4</sub>, supporting the mechanism for further enchainment and chain transfer processes shown in Scheme 1-2, steps ii and v. (Table 2-1, entries 7-11; Figure 2-2b). Further mechanistic insights will be offered in the Discussion section below.

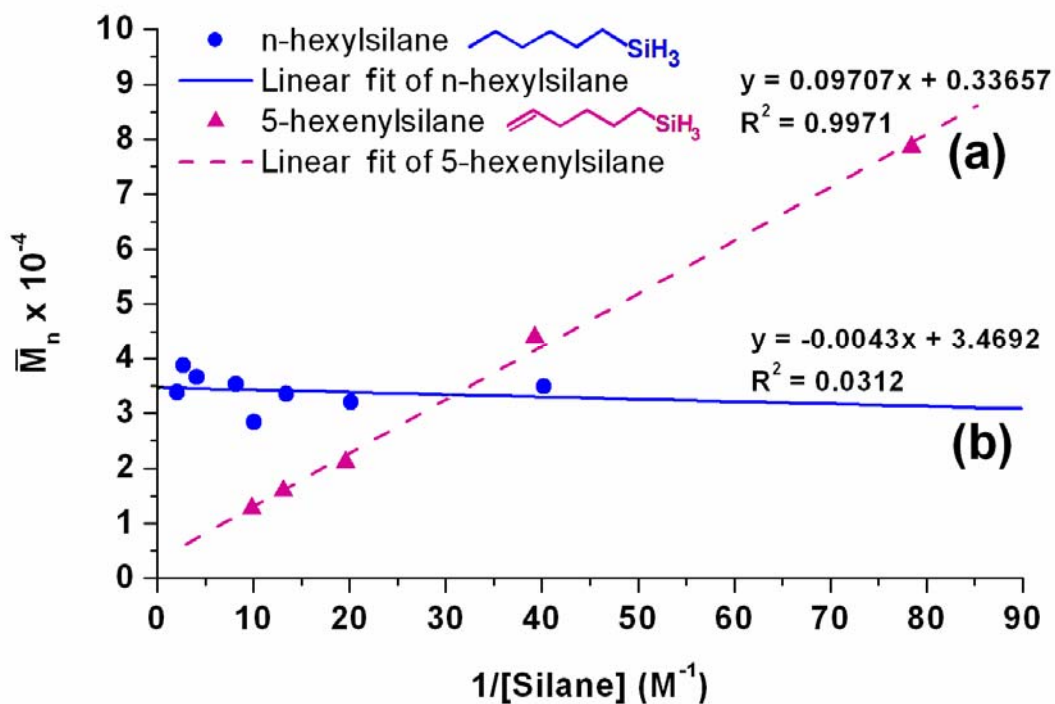
To better realize the role of the olefinic moiety in 5-hexenylsilane copolymerizations, a series of control ethylene polymerizations was performed in the presence of *n*-hexylsilane (Table 2-2). Note that here the chain transfer plot for *n*-hexylsilane in place of 5-hexenylsilane (Figure 2-3b) has a near-zero slope, indicating that *n*-hexylsilane functions as a *highly inefficient* chain transfer agent. In addition, the product <sup>1</sup>H NMR resonances at δ 5.0 and δ 5.5 indicate the presence of vinylic end groups in the polymer microstructure.

**Table 2-2.** Organotitanium—Catalyzed Ethylene Polymerization in the Presence of *n*-Hexylsilane

| Entry | Precatalyst <sup>a, b</sup> | [Precat.] (μM) | [C <sub>6</sub> H <sub>13</sub> SiH <sub>3</sub> ] (mM) | Activity <sup>c</sup> (x10 <sup>4</sup> ) | M <sub>n</sub> <sup>d</sup> | M <sub>w</sub> /M <sub>n</sub> <sup>d</sup> | T (°C) | T <sub>m</sub> (°C) |
|-------|-----------------------------|----------------|---------------------------------------------------------|-------------------------------------------|-----------------------------|---------------------------------------------|--------|---------------------|
| 1     | CGCTiMe <sub>2</sub>        | 200            | 24.9                                                    | 950                                       | 34900                       | 2.7                                         | 32     | 144                 |
| 2     | CGCTiMe <sub>2</sub>        | 200            | 49.7                                                    | 1100                                      | 32000                       | 3.0                                         | 28     | 144                 |
| 3     | CGCTiMe <sub>2</sub>        | 200            | 74.6                                                    | 900                                       | 33500                       | 2.8                                         | 33     | 143                 |
| 4     | CGCTiMe <sub>2</sub>        | 200            | 99.4                                                    | 850                                       | 28400                       | 3.3                                         | 34     | 142                 |
| 5     | CGCTiMe <sub>2</sub>        | 200            | 122                                                     | 1000                                      | 35300                       | 2.1                                         | 34     | 144                 |
| 6     | CGCTiMe <sub>2</sub>        | 200            | 245                                                     | 300                                       | 36600                       | 2.8                                         | 33     | 141                 |
| 7     | CGCTiMe <sub>2</sub>        | 200            | 367                                                     | 100                                       | 38700                       | 3.0                                         | 28     | 144                 |
| 8     | CGCTiMe <sub>2</sub>        | 200            | 490                                                     | 40                                        | 33800                       | 2.9                                         | 26     | 144                 |

<sup>a</sup>CGC = Me<sub>2</sub>Si(Me<sub>4</sub>C<sub>5</sub>)(N<sup>t</sup>Bu), EBI = Ethylene-bridged bis(indenyl); polymerization conditions: 50 mL toluene, 2.0 min. <sup>b</sup>cocatalyst = 10 μmol Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> <sup>c</sup>Units = g/(mol Ti • hr • atm ethylene) <sup>d</sup>By GPC in 1,2,4-trichlorobenzene vs. polyethylene standards

**Figure 2-3.** Relationship of polyethylene number average molecular weight (GPC versus polyethylene) to: (a) inverse  $C_6H_{11}SiH_3$  concentration at fixed catalyst and ethylene concentrations, and (b) inverse  $n\text{-}C_6H_{13}SiH_3$  concentration at fixed catalyst and ethylene concentrations.



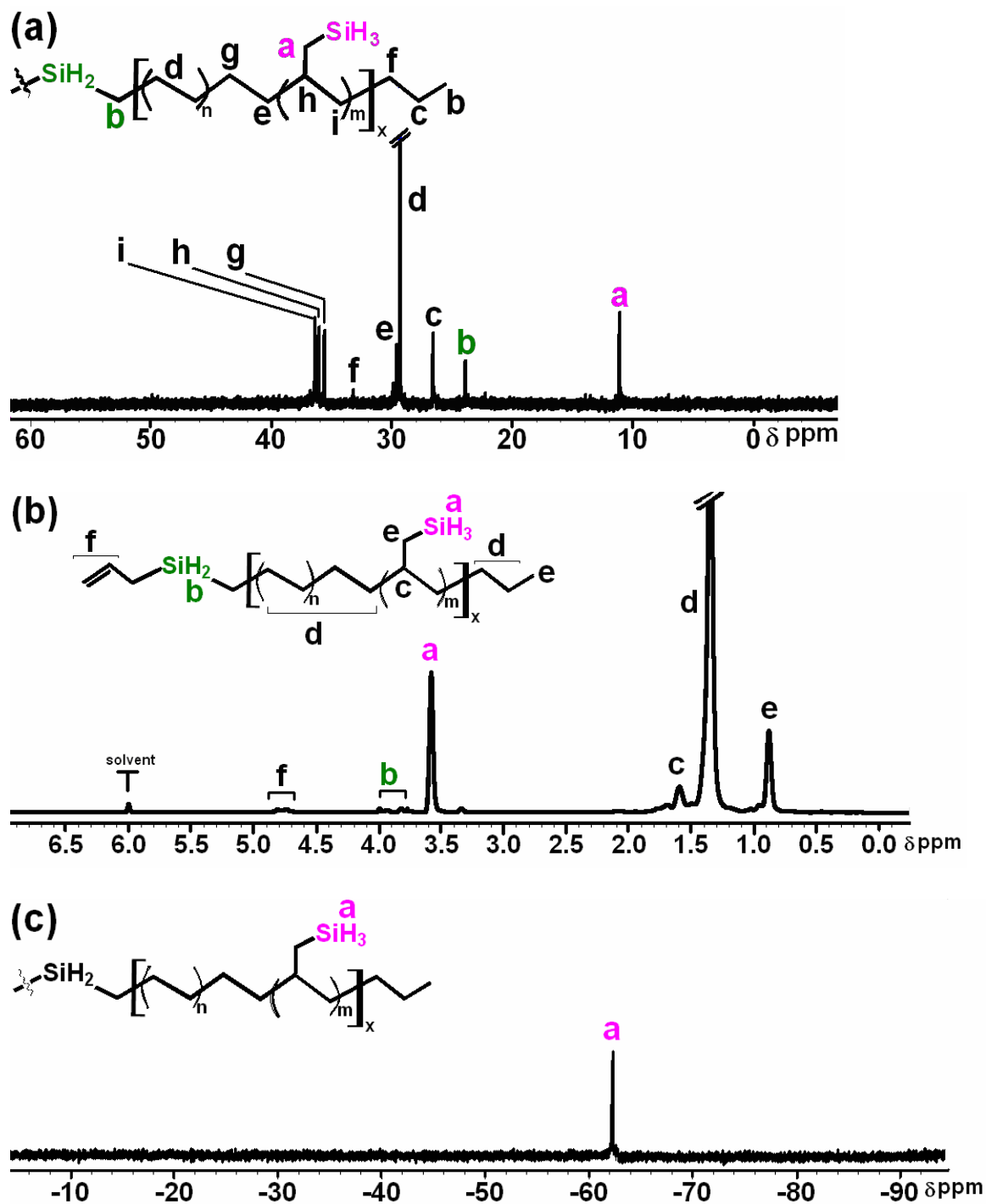
**Chain Transfer Efficiency of Allylsilane in Organotitanium-Mediated Ethylene Copolymerizations.** Allylsilane was also investigated as a comonomer/chain transfer agent for ethylene polymerization using organotitanium catalysts (Table 2-3). The  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR spectra of the silane-terminated ethylene + allylsilane copolymers reveal characteristic proton methylsilane branch ( $\delta$  0.88, 1.60, 3.58), polyethylene backbone ( $\delta$  1.2-1.5), and  $-\text{CH}_3$  chain end ( $\delta$  0.96) resonances (Figure 2-4). The concentration of vinyl chain end resonances is extremely small in the  $^1\text{H}$  NMR spectrum, indicating that chain transfer via  $\beta$ -hydride elimination is insignificant and that allylsilane chain termination is the dominant chain termination pathway. Furthermore, the strong  $-\text{SiH}_3$  resonance in the  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectra suggests that allylsilane readily undergoes insertion into the polymer chain in addition to effecting chain transfer at the polymer chain end. In addition, the resulting allylsilane-capped copolymers have narrow, monomodal polydispersities consistent with a single-site polymerization process, and a strong  $^{29}\text{Si}$  NMR resonance at  $\delta$  -62.3 ppm, consistent with an  $-\text{SiH}_3$  silicon environment, indicating significant amounts of methylsilane branches. The  $^{13}\text{C}$  NMR and GPC-MALLS data (see below) indicate approximately 150 methylsilane branches per 1000 carbon atoms. The copolymer melting temperatures are 10-15  $^\circ\text{C}$  lower than that of ethylene homopolymers produced by the same catalysts (Table 2-4, entries 2-3), suggesting considerable quantities of short- and long-chain branching.

**Table 2-3.** Organotitanium—Catalyzed Ethylene Polymerization in the Presence of Allylsilane

| Entry | Precatalyst <sup>a, b</sup>           | [Precat.] (μM) | [C <sub>3</sub> H <sub>5</sub> SiH <sub>3</sub> ] (mM) | Activity <sup>c</sup> (x10 <sup>4</sup> ) | M <sub>n</sub> <sup>d</sup> | M <sub>w</sub> /M <sub>n</sub> <sup>d</sup> | T (°C) | T <sub>m</sub> (°C) | comonomer incorporation % <sup>e</sup> |
|-------|---------------------------------------|----------------|--------------------------------------------------------|-------------------------------------------|-----------------------------|---------------------------------------------|--------|---------------------|----------------------------------------|
| 1     | CGCTiMe <sub>2</sub>                  | 200            | 24.2                                                   | 2600                                      | 10100                       | 2.3                                         | 27     | 132                 | 32                                     |
| 2     | CGCTiMe <sub>2</sub>                  | 200            | 48.4                                                   | 2700                                      | 5400                        | 3.2                                         | 28     | 130                 | 34                                     |
| 3     | CGCTiMe <sub>2</sub>                  | 200            | 121                                                    | 1700                                      | 3610                        | 3.6                                         | 30     | 130                 | 54                                     |
| 4     | CGCTiMe <sub>2</sub>                  | 200            | 169                                                    | 3000                                      | 3220                        | 4.0                                         | 30     | 128                 | 52                                     |
| 5     | CGCTiMe <sub>2</sub>                  | 200            | 217                                                    | 3500                                      | 2680                        | 4.0                                         | 33     | 130                 | 50                                     |
| 6     | CGCTiMe <sub>2</sub>                  | 200            | 362                                                    | 3300                                      | 2350                        | 3.6                                         | 35     | 131                 | 52                                     |
| 7     | CGCTiMe <sub>2</sub>                  | 200            | 484                                                    | 2200                                      | 1100                        | 2.0                                         | 23     | 127                 | 52                                     |
| 8     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 24.2                                                   | 760                                       | 23300                       | 3.1                                         | 30     | 129                 | 4.0                                    |
| 9     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 48.4                                                   | 670                                       | 16400                       | 2.4                                         | 30     | 128                 | 5.0                                    |
| 10    | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 121                                                    | 500                                       | 14400                       | 2.4                                         | 25     | 128                 | 12                                     |
| 11    | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 169                                                    | 500                                       | 9700                        | 3.2                                         | 25     | 130                 | 32                                     |
| 12    | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 217                                                    | 40                                        | 9100                        | 3.5                                         | 30     | 127                 | 28                                     |
| 13    | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 362                                                    | 10                                        | 6300                        | 4.2                                         | 25     | 129                 | 32                                     |
| 14    | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 484                                                    | 10                                        | 1100                        | 1.1                                         | 23     | 127                 | 30                                     |

<sup>a</sup>CGC = Me<sub>2</sub>Si(Me<sub>4</sub>C<sub>5</sub>)(N<sup>t</sup>Bu), EBI = Ethylene-bridged bis(indenyl); polymerization conditions: 50 mL toluene, 10 sec. for entries 1-7, 10 min. for entries 8-14 <sup>b</sup> cocatalyst = 10 μmol Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> <sup>c</sup>Units = g/(mol Ti • hr • atm ethylene) <sup>d</sup>By GPC in 1,2,4-trichlorobenzene vs. polyethylene standards <sup>e</sup> comonomer incorporation calculated based on <sup>13</sup>C NMR spectra.

**Figure 2-4.** (a)  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum, (b)  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum, and (c)  $^{29}\text{Si}$  NMR (75.5 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum of the ethylene + allylsilane copolymer produced by  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ .



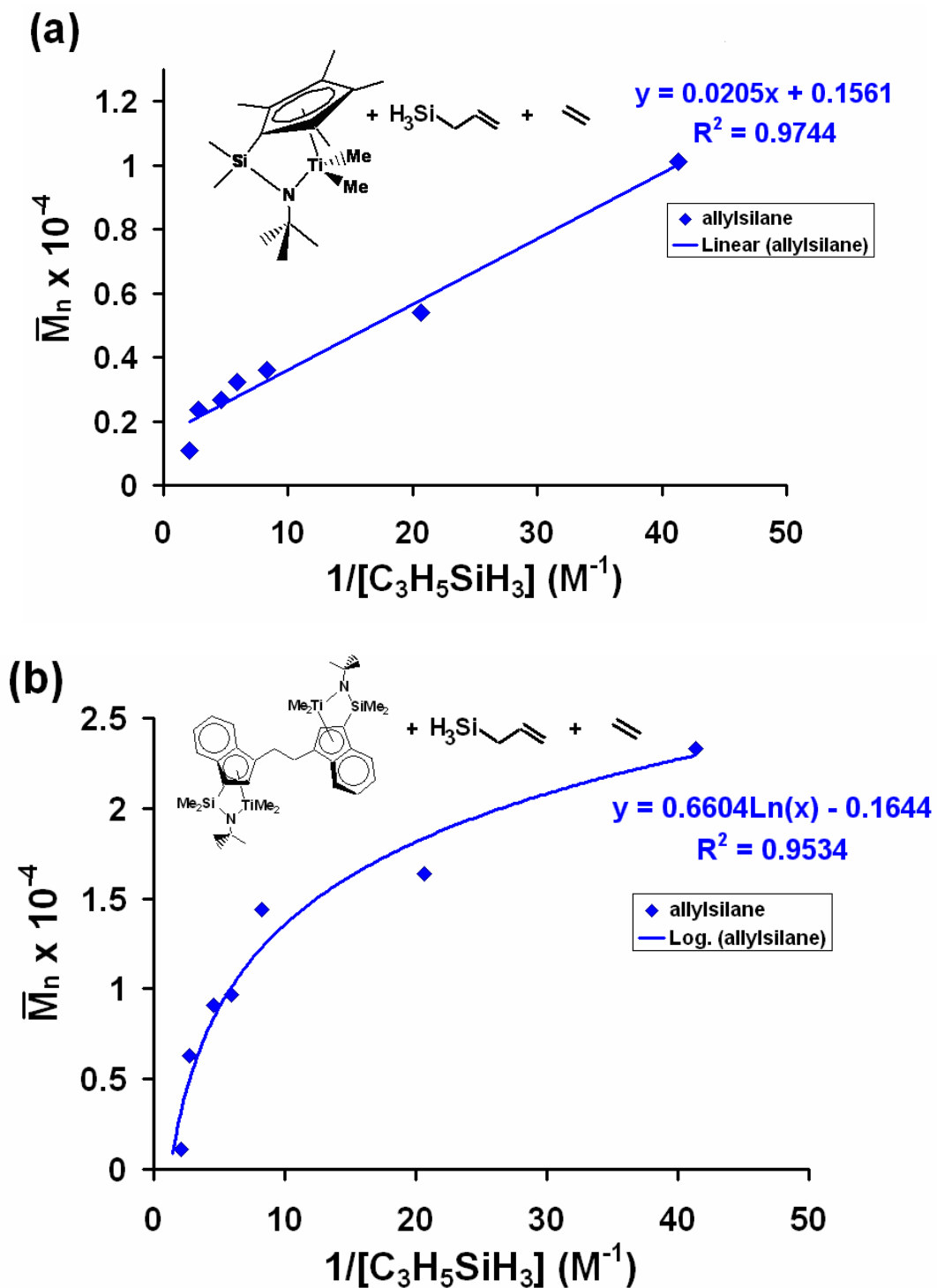
**Table 2-4.** Organotitanium—Catalyzed Ethylene Homopolymerization

| Entry | Precatalyst <sup>a, b</sup>           | [Precat.] (μM) | Activity <sup>c</sup> (×10 <sup>4</sup> ) | M <sub>n</sub> <sup>d</sup> | M <sub>w</sub> /M <sub>n</sub> <sup>d</sup> | T (°C) | T <sub>m</sub> (°C) |
|-------|---------------------------------------|----------------|-------------------------------------------|-----------------------------|---------------------------------------------|--------|---------------------|
| 1     | Cp*TiMe <sub>3</sub>                  | 200            | 500                                       | 27700                       | 2.8                                         | 30     | 141                 |
| 2     | CGCTiMe <sub>2</sub>                  | 200            | 210                                       | 102800                      | 2.6                                         | 32     | 142                 |
| 3     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 200                                       | 150000                      | 2.5                                         | 28     | 144                 |

<sup>a</sup>CGC = Me<sub>2</sub>Si(Me<sub>4</sub>C<sub>5</sub>)(N<sup>t</sup>Bu), EBI = Ethylene-bridged bis(indenyl); polymerization conditions: 50 mL toluene, 0.5 min. <sup>b</sup> cocatalyst = 10 μmol Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> <sup>c</sup>Units = g/(mol Ti • hr • atm ethylene) <sup>d</sup>By GPC in 1,2,4-trichlorobenzene vs. polyethylene standards

For polymerizations conducted in the presence of allylsilane, titanium nuclearity and polymer molecular weight are linearly related. However, ethylene/allylsilane polymerizations mediated by  $\text{EBICGCTi}_2\text{Me}_4/2\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  require longer reaction times as compared to mononuclear organotitanium-mediated systems, to produce significant amounts of polymer with useful molecular weight ( $M_n = 14400$ ; Table 2-3, entry 10). In contrast,  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -mediated polymerizations result in copolymers of lower molecular weight ( $M_n = 3610$ ; Table 2-3, entry 3) but with significantly higher activities ( $10^7$  g polymer/(mol Ti • atm ethylene • h)) and with appreciably greater comonomer incorporation. After catalyst injection into the polymerization reactor, both mono- and binuclear Ti catalyst solutions remain brightly colored, implying the presence of stable active catalytic species.<sup>12c,15j</sup> At constant catalyst and ethylene concentrations, product copolymer molecular weight is inversely proportional to silane concentration for  $\text{CGCTiMe}_2$  (Table 2-3, entries 1-7; Figure 2-5a), supporting the chain transfer mechanism depicted in Scheme 1-2. Intriguingly, under similar conditions, product copolymer molecular weight decreases approximately sublinearly with increasing silane concentration for  $\text{EBICGCTi}_2\text{Me}_4$  (Table 2-3, entries 8-14; Figure 2-5b). These chain transfer relationships suggest a distinctly different overall mechanistic pathway for polymerization with the bimetallic Ti catalyst, which will be elaborated on in the Discussion section.

**Figure 2-5.** Relationship of ethylene + allylsilane copolymer number-average molecular weight (GPC vs. polyethylene standards) to inverse allylsilane concentration at fixed ethylene and (a) CGCTiMe<sub>2</sub> (b) EBICGCTi<sub>2</sub>Me<sub>4</sub> concentrations.



**Chain Transfer Efficiency of 3-Butenylsilane in Organotitanium-Mediated Ethylene Copolymerizations.** The comonomer 3-butenylsilane was also investigated as a chain transfer agent for ethylene copolymerization in the presence of mono- and binuclear organotitanium catalysts (Table 2-5). The  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR spectra of the silane-terminated ethylene/3-butenylsilane copolymers exhibit characteristic proton ethylsilane branch ( $\delta$  0.46, 1.98, 3.59), polyethylene backbone ( $\delta$  1.2-1.4), and  $-\text{CH}_3$  chain end ( $\delta$  0.98) resonances (Figure 2-6). The concentrations of vinyl chain end resonances are again small in the  $^1\text{H}$  NMR spectrum, indicating that chain transfer via  $\beta$ -hydride elimination is inconsequential and that 3-butenylsilane chain termination is the dominant chain transfer pathway. Furthermore, the intense  $-\text{SiH}_2-$  resonance in the  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectra suggests that 3-butenylsilane readily effects chain transfer at the polymer chain end as well as at the branch points, in addition to undergoing  $\text{C}=\text{C}$  enchainment into the polymer chain.

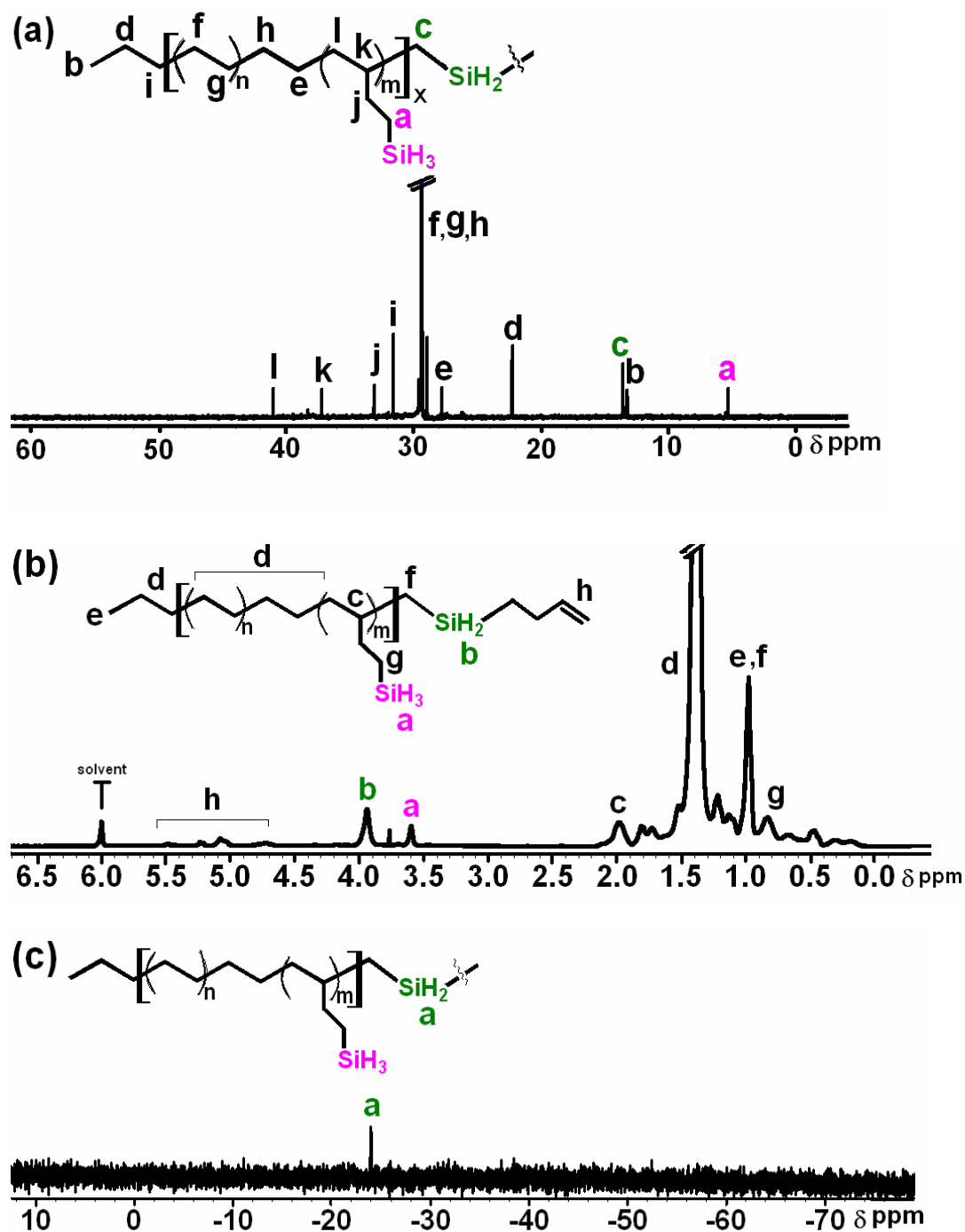
In addition, the resulting 3-butenylsilane-capped copolymers have narrow, monomodal polydispersities consistent with a single-site process and exhibit a strong  $-\text{SiH}_2-$   $^{29}\text{Si}$  NMR resonance at  $\delta$  -24.0 ppm, indicating that significant fractions of ethylsilane branches have likely chain transferred to additional polymer chains. The  $^{13}\text{C}$  NMR and GPC-MALLS data indicate approximately 50 ethylsilane branches per 1000 carbon atoms. The polymer melting temperatures are considerably lower (20-40  $^\circ\text{C}$ ) than that of the ethylene homopolymer produced with the same catalysts (Table 2-4, entries 2-3), implying a significant degree of longer-chain branching in the copolymer products.

**Table 2-5.** Organotitanium—Catalyzed Ethylene Polymerization in the Presence of 3-Butenylsilane

| Entry | Precatalyst <sup>a, b</sup>           | [Precat.] (μM) | [C <sub>4</sub> H <sub>7</sub> SiH <sub>3</sub> ] (mM) | Activity <sup>c</sup> (x10 <sup>4</sup> ) | M <sub>n</sub> <sup>d</sup> | M <sub>w</sub> /M <sub>n</sub> <sup>d</sup> | T (°C) | T <sub>m</sub> (°C) | comonomer incorporation (%) <sup>e</sup> |
|-------|---------------------------------------|----------------|--------------------------------------------------------|-------------------------------------------|-----------------------------|---------------------------------------------|--------|---------------------|------------------------------------------|
| 1     | CGCTiMe <sub>2</sub>                  | 200            | 15.8                                                   | 2000                                      | 9800                        | 2.4                                         | 30     | 121                 | 5.0                                      |
| 2     | CGCTiMe <sub>2</sub>                  | 200            | 31.5                                                   | 1600                                      | 3000                        | 3.1                                         | 32     | 115                 | 12                                       |
| 3     | CGCTiMe <sub>2</sub>                  | 200            | 78.9                                                   | 1200                                      | 2600                        | 3.5                                         | 34     | 112                 | 20                                       |
| 4     | CGCTiMe <sub>2</sub>                  | 200            | 110                                                    | 1900                                      | 2300                        | 4.2                                         | 32     | 112                 | 20                                       |
| 5     | CGCTiMe <sub>2</sub>                  | 200            | 142                                                    | 1600                                      | 980                         | 1.5                                         | 33     | 110                 | 22                                       |
| 6     | CGCTiMe <sub>2</sub>                  | 200            | 237                                                    | 440                                       | 610                         | 1.3                                         | 30     | 106                 | 23                                       |
| 7     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 15.8                                                   | 6.0                                       | 104300                      | 1.4                                         | 24     | 130                 | 1.0                                      |
| 8     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 31.5                                                   | 1.0                                       | 92000                       | 1.4                                         | 23     | 130                 | 1.0                                      |
| 9     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 78.9                                                   | 0.1                                       | 88000                       | 2.0                                         | 24     | 131                 | 5.0                                      |
| 10    | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 110                                                    | 0.02                                      | 82000                       | 2.0                                         | 22     | 127                 | 5.0                                      |
| 11    | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 142                                                    | 0.02                                      | 55700                       | 2.7                                         | 23     | 128                 | 5.0                                      |
| 12    | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 237                                                    | 0.02                                      | 45600                       | 3.2                                         | 27     | 126                 | 7.0                                      |

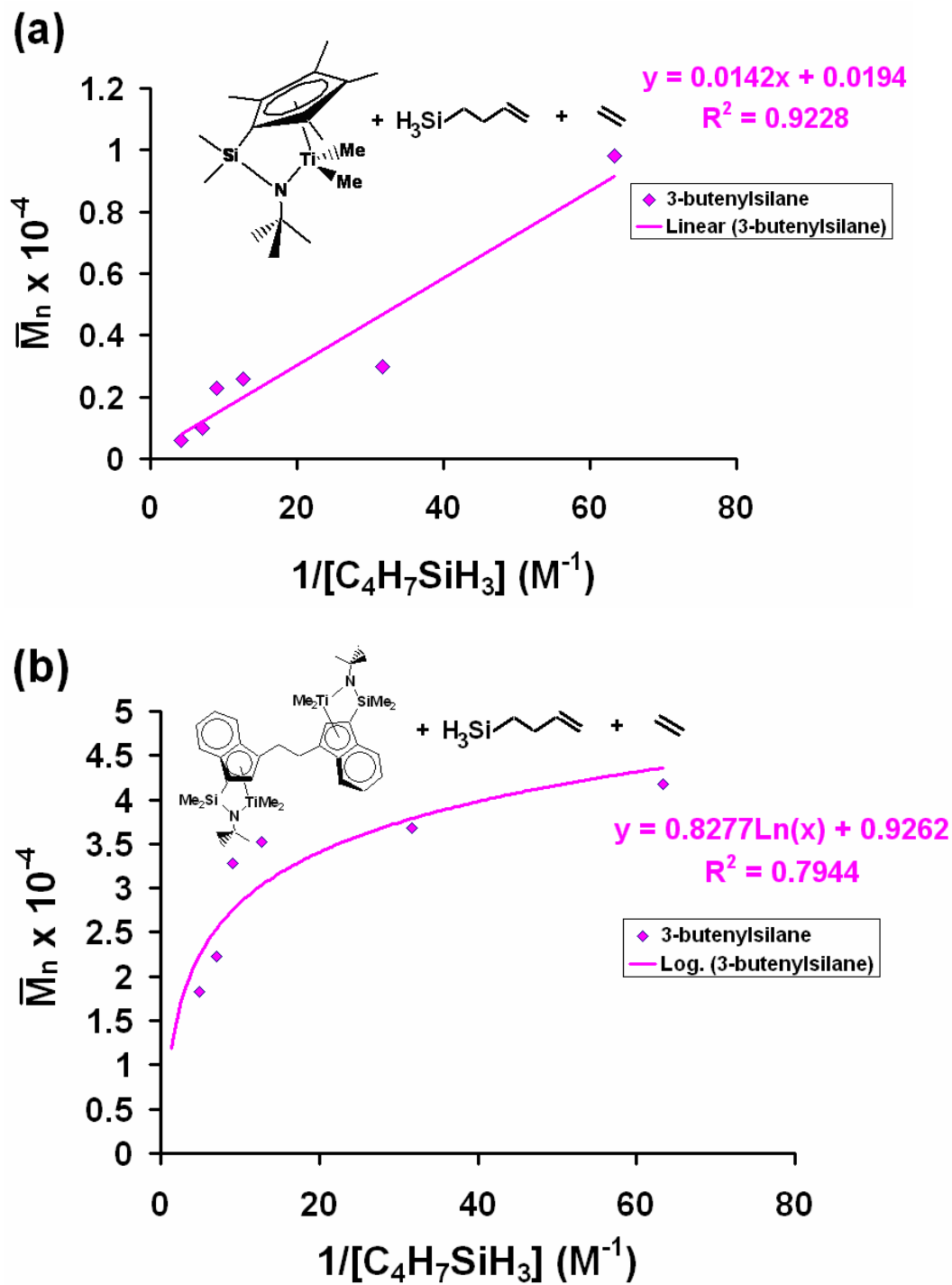
<sup>a</sup>CGC = Me<sub>2</sub>Si(Me<sub>4</sub>C<sub>5</sub>)(N<sup>t</sup>Bu), EBI = Ethylene-bridged bis(indenyl); polymerization conditions: 50 mL toluene, 10 sec. for entries 1-6, 10 min. for entries 7-12 <sup>b</sup> cocatalyst = 10 μmol Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> <sup>c</sup>Units = g/(mol Ti • hr • atm ethylene) <sup>d</sup>By GPC in 1,2,4-trichlorobenzene vs. polyethylene standards <sup>e</sup> comonomer incorporation calculated based on <sup>13</sup>C NMR spectra.

**Figure 2-6.** (a)  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum, (b)  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum, and (c)  $^{29}\text{Si}$  NMR (75.5 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum of the ethylene/3-butenylsilane copolymer produced by  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ .



Interestingly, for polymerizations conducted in the presence of 3-butenylsilane, titanium nuclearity and polymer molecular weight are linearly correlated as in the case of allylsilane. Thus, ethylene/3-butenylsilane polymerizations mediated by EBICGCTi<sub>2</sub>Me<sub>4</sub>/2Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> require longer reaction times compared to mononuclear organotitanium-mediated systems, to produce considerable amounts of polymer, but having much higher molecular weights ( $M_n = 82000$ ; Table 2-5, entry 10). On the other hand, CGCTiMe<sub>2</sub>/Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>-mediated polymerizations result in copolymers with substantially lower molecular weights ( $M_n = 2300$ ; Table 2-5, entry 4) but at significantly higher activities ( $10^7$  g polymer/(mol Ti • atm ethylene • h)) and with far greater comonomer incorporation levels. After catalyst injection into the polymerization reactor, both mono- and binuclear Ti catalysts remain brightly colored, implying the presence of active catalytic species.<sup>12c,15j</sup> At constant catalyst and ethylene concentrations, product copolymer molecular weight is inversely proportional to silane concentration for CGCTiMe<sub>2</sub> (Table 2-5, entries 1-6; Figure 2-7a), supporting the chain transfer mechanism shown in Scheme 2-2. Interestingly, under similar conditions, product copolymer molecular weight decreases approximately sublinearly with increasing silane concentration for polymerizations mediated by EBICGCTi<sub>2</sub>Me<sub>4</sub> (Table 2-5, entries 7-12; Figure 2-7b), supporting a cooperative mechanism that enhances chain transfer efficiency at higher silane concentrations. These chain transfer relationships suggest a significantly different mechanistic pathway for polymerization with the bimetallic Ti catalyst, which will be elaborated on in the Discussion section.

**Figure 2-7.** Relationship of ethylene + 3-butenylsilane copolymer number-average molecular weight (GPC vs. polyethylene standards) to inverse 3-butenylsilane concentration at fixed ethylene and (a) CGCTiMe<sub>2</sub> (b) EBICGCTi<sub>2</sub>Me<sub>4</sub> concentrations.



**Chain Transfer Efficiency of 7-Octenylsilane in Organotitanium-Mediated Ethylene Copolymerizations.** The comonomer 7-octenylsilane was also investigated as a chain transfer agent for ethylene polymerization using both mono- and binuclear organotitanium catalysts (Table 2-6). The  $^1\text{H}$  NMR spectra of the silane-terminated ethylene/7-octenylsilane copolymers exhibit characteristic proton hexylsilane branch ( $\delta$  0.28, 2.15, 3.59), polyethylene backbone ( $\delta$  1.2-1.4), and  $-\text{CH}_3$  chain end ( $\delta$  0.97) resonances (Figure 2-8). The concentrations of vinyl chain end resonances are below the detection limits in both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, signifying that chain transfer via  $\beta$ -hydride elimination is again inconsequential and that intramolecular 7-octenylsilane chain termination is the dominant chain transfer pathway. Furthermore, the intense  $-\text{SiH}_2$  and  $-\text{SiH}$  resonances in the  $^1\text{H}$  NMR spectrum suggest that 7-octenylsilane readily effects chain transfer at the polymer chain end as well as at the branch points, in addition to undergoing  $\text{C}=\text{C}$  enchainment into the polymer chain. The resulting 7-octenylsilane-capped copolymers have narrow, monomodal polydispersities consistent with a single-site process and prominent  $^1\text{H}$  NMR resonances at  $\delta$  3.59 ( $-\text{SiH}_3$ ), 3.95 ( $-\text{SiH}_2-$ ), and 4.70 ( $>\text{SiH}-$ ) ppm indicating that small but significant quantities of hexylsilane branches have chain transferred to additional polymer chains. In addition, the  $^1\text{H}$  NMR and GPC-MALLS data indicate approximately 10 hexylsilane branches per 1000 carbon atoms. The copolymer melting temperatures are significantly lower (20-40  $^\circ\text{C}$ ) than that of the ethylene homopolymer produced with the same catalysts (Table 2-4, entries 2-3), implying a considerable degree of longer-chain branching in the copolymer products.

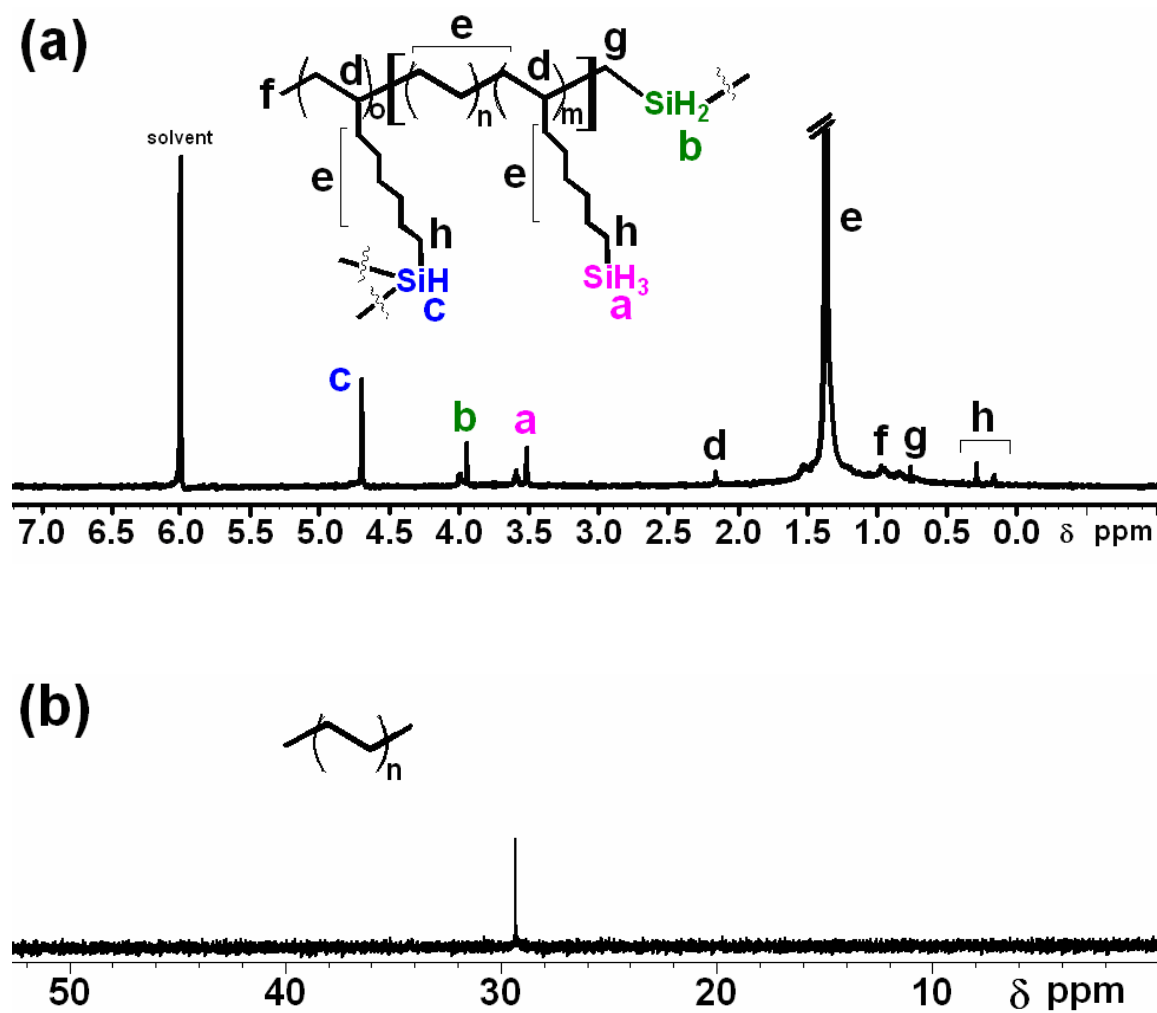
**Table 2-6.** Organotitanium—Catalyzed Ethylene Polymerization in the Presence of 7-Octenylsilane

| Entry | Precatalyst <sup>a, b</sup>           | [Precat.] (μM) | [C <sub>8</sub> H <sub>15</sub> SiH <sub>3</sub> ] (mM) | Activity <sup>c</sup> (x10 <sup>4</sup> ) | M <sub>n</sub> <sup>d</sup> | M <sub>w</sub> /M <sub>n</sub> <sup>d</sup> | T (°C) | T <sub>m</sub> (°C) | comonomer incorporation % <sup>e</sup> |
|-------|---------------------------------------|----------------|---------------------------------------------------------|-------------------------------------------|-----------------------------|---------------------------------------------|--------|---------------------|----------------------------------------|
| 1     | CGCTiMe <sub>2</sub>                  | 200            | 20.2                                                    | 290                                       | 5600                        | 2.9                                         | 30     | 120                 | 0.5                                    |
| 2     | CGCTiMe <sub>2</sub>                  | 200            | 40.4                                                    | 10                                        | 7200                        | 2.5                                         | 25     | 116                 | 1.0                                    |
| 3     | CGCTiMe <sub>2</sub>                  | 200            | 60.6                                                    | 35                                        | 7600                        | 2.1                                         | 25     | 122                 | 3.0                                    |
| 4     | CGCTiMe <sub>2</sub>                  | 200            | 101                                                     | 0.2                                       | 8400                        | 2.5                                         | 28     | 122                 | 4.0                                    |
| 5     | CGCTiMe <sub>2</sub>                  | 200            | 141                                                     | 0.3                                       | 10700                       | 2.6                                         | 24     | 126                 | 4.0                                    |
| 6     | CGCTiMe <sub>2</sub>                  | 200            | 182                                                     | 0.2                                       | 16000                       | 3.5                                         | 24     | 124                 | 5.0                                    |
| 7     | CGCTiMe <sub>2</sub>                  | 200            | 220                                                     | 0.2                                       | 17200                       | 2.2                                         | 24     | 123                 | 5.0                                    |
| 8     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 20.2                                                    | 2.0                                       | 4500                        | 2.0                                         | 24     | 106                 | 0.5                                    |
| 9     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 40.4                                                    | 0.1                                       | 5000                        | 2.4                                         | 24     | 110                 | 1.0                                    |
| 10    | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 60.6                                                    | 0.2                                       | 5300                        | 2.5                                         | 26     | 107                 | 1.0                                    |
| 11    | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 101                                                     | 0.1                                       | 6000                        | 2.4                                         | 25     | 100                 | 2.0                                    |
| 12    | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 100            | 141                                                     | 0.4                                       | 10000                       | 2.1                                         | 25     | 101                 | 2.0                                    |

<sup>a</sup>CGC = Me<sub>2</sub>Si(Me<sub>4</sub>C<sub>5</sub>)(N<sup>t</sup>Bu), EBI = Ethylene-bridged bis(indenyl); polymerization conditions: 50 mL toluene, 10 min. for entries 1-7, 60 min. for entries 8-12

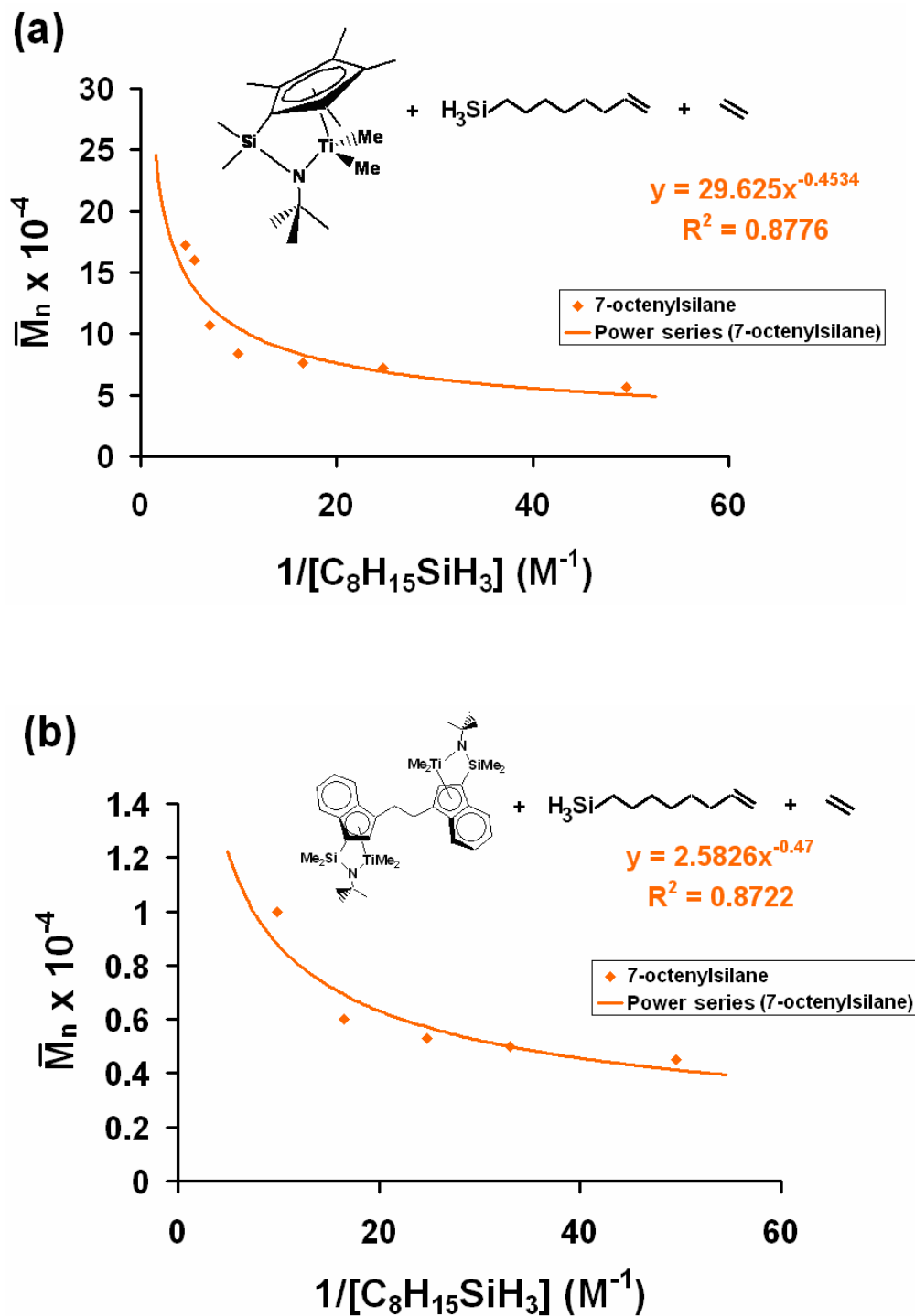
<sup>b</sup> cocatalyst = 10 μmol Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> <sup>c</sup>Units = g/(mol Ti • hr • atm ethylene) <sup>d</sup>By GPC in 1,2,4-trichlorobenzene vs. polyethylene standards <sup>e</sup> comonomer incorporation calculated based on <sup>13</sup>C NMR spectra.

**Figure 2-8.** (a)  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum, (b)  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum of the ethylene + 7-octenylsilane copolymer produced by  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ .



For polymerizations conducted in the presence of 7-octenylsilane, titanium nuclearity and polymer molecular weight are inversely correlated. Ethylene/7-octenylsilane polymerizations mediated by  $\text{EBICGCTi}_2\text{Me}_4/2\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  require longer reaction times compared to the mononuclear organotitanium-mediated systems, to produce considerable amounts of polymer with lower molecular weights ( $M_n = 6000$ ; Table 2-6, entry 11). In contrast,  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -mediated polymerizations result in copolymers with higher molecular weights ( $M_n = 8400$ ; Table 2-6, entry 4) at significantly higher activities ( $10^5$  g polymer/(mol Ti • atm ethylene • h)) and with greater comonomer enchainment selectivities. After catalyst injection into the polymerization reactor, both mono- and binuclear Ti catalysts remain brightly colored, implying the presence of active catalytic species.<sup>12c,15j</sup> At constant catalyst and ethylene concentrations, product copolymer molecular weight increases as an approximate superlinear series with increasing silane concentration for  $\text{CGCTiMe}_2$  (Table 2-6, entries 1-7; Figure 2-9a), suggesting more long-chain branching at higher silane concentrations, which increases the polymer molecular weight. Interestingly, under similar conditions, product copolymer molecular weight also increases as an approximate superlinear series with increasing silane concentration for polymerizations mediated by  $\text{EBICGCTi}_2\text{Me}_4$  (Table 2-6, entries 8-12; Figure 2-9b). The chain transfer plots in addition to the  $^1\text{H}$  NMR resonances at  $\delta$  3.95 and 4.70 ppm indicate the presence of considerable quantities of hexylsilane branches which have chain transferred additional polymer chains. These plots again suggest a different overall mechanistic pathway for polymerization/chain transfer mediated by the bimetallic Ti catalyst as well as for longer alkenylsilanes, which will be analyzed in the Discussion section.

**Figure 2-9.** Relationship of ethylene + 7-octenylsilane copolymer number-average molecular weight (GPC vs. polyethylene standards) to inverse 7-octenylsilane concentration at fixed ethylene and (a) CGCTiMe<sub>2</sub> (b) EBICGCTi<sub>2</sub>Me<sub>4</sub> concentrations.



**Summary of the Scope of Alkenylsilane Chain Transfer and Comonomer Effects in Organotitanium-Mediated Ethylene Polymerization.** Organotitanium complexes catalyze the copolymerization of alkenylsilanes + ethylene with high activity. However, the product polymer microstructures and the chain transfer behavior of the various alkenylsilanes are highly dependent on both the alkenylsilane chain length and Ti catalyst nuclearity. In all of these polymerization systems, polymer molecular weights differ drastically from the corresponding ethylene homopolymerizations, ethylene/1-hexene copolymerizations, and ethylene homopolymerization in the presence of *n*-hexylsilane carried out with the same organotitanium catalysts. For all alkenylsilane + ethylene copolymers produced, alkenylsilane chain transfer is the dominant chain termination pathway as indicated by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR spectroscopy and chain transfer plots (Figures (2-1)–(2-9)).

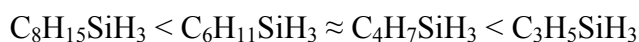
**Mechanistic Considerations.** As a prelude to a detailed discussion of alkenylsilane + ethylene copolymerization mechanism and kinetics, it is useful to briefly summarize the relevant observations.

- (i) Mononuclear activated  $\text{CGCTiMe}_2$  mediates ideally-behaved silanolytic chain transfer, indicated by the linear relationship between  $M_n$  and  $[\text{alkenylsilane}]^{-1}$  for  $\text{C}_3$  to  $\text{C}_6$  alkenylsilanes.
- (ii) Binuclear activated  $\text{EBICGCTi}_2\text{Me}_4$  mediates less than ideally-behaved silanolytic chain transfer, indicated by the sublinear relationship between  $M_n$  and  $[\text{alkenylsilane}]^{-1}$  for  $\text{C}_3$  and  $\text{C}_4$  alkenylsilanes.

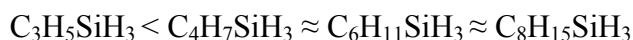
- (iii) Binuclear activated EBICGCTi<sub>2</sub>Me<sub>4</sub> mediates less than ideal silanolytic chain transfer, indicated by the superlinear relationship between  $M_n$  and [alkenylsilane]<sup>-1</sup> for C<sub>6</sub> and C<sub>8</sub> alkenylsilanes.
- (iv) All organotitanium systems efficiently produce silane-capped polyolefins.
- (v) Binuclear EBICGCTi<sub>2</sub>Me<sub>4</sub> generally produces higher molecular weight polymer versus mononuclear CGCTiMe<sub>2</sub> for all of the alkenylsilanes.
- (vi) Mononuclear CGCTiMe<sub>2</sub> consistently incorporates higher levels of comonomer versus binuclear EBICGCTi<sub>2</sub>Me<sub>4</sub> for all of the alkenylsilanes.
- (vii) As alkenylsilane chain length increases, the level of comonomer incorporation parallels that of the analogous  $\alpha$ -olefin + ethylene copolymerizations.<sup>21</sup>
- (viii) As C<sub>3</sub> and C<sub>4</sub> [alkenylsilane] increases, polyolefin molecular weight decreases for all organotitanium-mediated systems.
- (ix) As [5-hexenylsilane] increases, polyolefin molecular weight decreases for CGCTiMe<sub>2</sub>-mediated systems and increases for EBICGCTi<sub>2</sub>Me<sub>4</sub>-mediated systems.
- (x) As [7-octenylsilane] increases, polyolefin molecular weight increases for all organotitanium-mediated systems.

## Discussion

**Effects of Alkenylsilane Chain Dimensions on Comonomer Incorporation and Branch Formation.** The present results indicate that the extent of alkenylsilane incorporation and branch formation during organotitanium-catalyzed copolymerization with ethylene increases in the order:



This is consistent with general literature precedent for unfunctionalized  $\alpha$ -olefin relative insertion rates.<sup>33</sup> The  $^{13}\text{C}$  NMR and GPC-MALLS-derived comonomer incorporation data are in good agreement. The GPC-MALLS-derived long-chain branching (LCB) data indicate that the ratio of LCB to total branch content increases in the order:



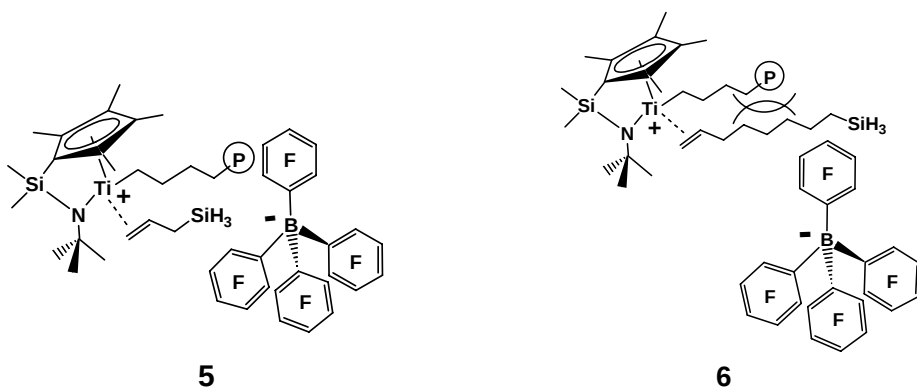
The smallest alkenylsilane, allylsilane, exhibits the greatest co-enchainment selectivity, resulting in approximately 150 total branches + 10 LCB and 100 total branches + 10 LCB per 1000 carbon atoms, for mono- and binuclear catalyst systems, respectively (Table 2-7, entries 1-2). The relatively high  $T_m$  of the allylsilane/ethylene copolymers is likely due to substantial blocks of enchainment allylsilane as well as some amount of crosslinking owing to the high  $-\text{SiH}_x$  concentrations. In comparison, 3-butenylsilane results in polyethylenes with approximately 50 total branches + 10 LCB and 20 total branches + 5 LCB per 1000 carbon atoms for mono- and binuclear systems, respectively (Table 2-7, entries 3-4). The mid-length 5-hexenylsilane results in polyethylenes with approximately 40 total branches + 10 LCB and 20 total branches + 5.0 LCB per 1000 carbon atoms for mono- and binuclear systems, respectively (Table 2-7, entries 5-6).

**Table 2-7.** GPC-MALLS-derived Branching Data for Organotitanium-Catalyzed Copolymerizations

| Entry | Precatalyst <sup>a, b</sup>           | Alkenylsilane   | [alkenylsilane]<br>(mM) | B per<br>1000 C <sup>c</sup> | LCB per<br>1000 C <sup>c</sup> | % LCB<br>per B <sup>c</sup> | RMS <sup>c</sup><br>(nm) | $g_M^c$ |
|-------|---------------------------------------|-----------------|-------------------------|------------------------------|--------------------------------|-----------------------------|--------------------------|---------|
| 1     | CGCTiMe <sub>2</sub>                  | allylsilane     | 121                     | 150 (35)                     | 10 (5)                         | 6.0 (3.0)                   | 78.5 (8.6)               | 0.1     |
| 2     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | allylsilane     | 121                     | 100 (13)                     | 10 (3)                         | 10 (2)                      | 38.0 (11)                | 0.1     |
| 3     | CGCTiMe <sub>2</sub>                  | 3-butenylsilane | 110                     | 50 (7)                       | 10 (2)                         | 20 (3)                      | 15.5 (2.3)               | 0.5     |
| 4     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 3-butenylsilane | 110                     | 20 (7)                       | 5.0 (1.5)                      | 25 (6)                      | 91.9 (23)                | 0.3     |
| 5     | CGCTiMe <sub>2</sub>                  | 5-hexenylsilane | 51.1                    | 40 (5)                       | 10 (3)                         | 25 (4)                      | 91.7 (18)                | 0.2     |
| 6     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 5-hexenylsilane | 51.1                    | 20 (7)                       | 5.0 (2.3)                      | 25 (7)                      | 115 (13)                 | 0.2     |
| 7     | CGCTiMe <sub>2</sub>                  | 7-octenylsilane | 101                     | 10 (3)                       | 2.0 (0.3)                      | 20 (3)                      | 88.7 (18)                | 1.0     |
| 8     | EBICGCTi <sub>2</sub> Me <sub>4</sub> | 7-octenylsilane | 101                     | 10 (3)                       | 2.0 (0.7)                      | 20 (5)                      | 80.7 (24)                | 1.0     |

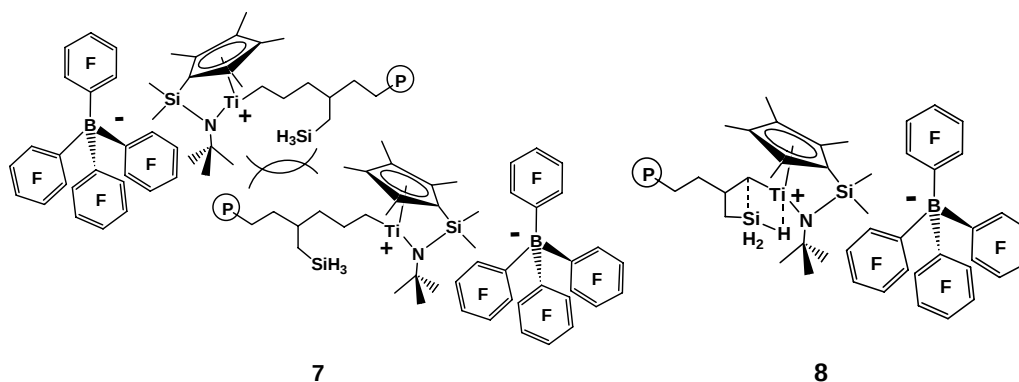
<sup>a</sup>CGC = Me<sub>2</sub>Si(Me<sub>4</sub>C<sub>5</sub>)(N<sup>t</sup>Bu), EBI = Ethylene-bridged bis(indenyl); [CGCTiMe<sub>2</sub>] = 200 μM, [EBICGCTi<sub>2</sub>Me<sub>4</sub>] = 100 μM <sup>b</sup> cocatalyst = 10 μmol Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> <sup>c</sup>B = total branches, C = carbon atoms, LCB = Long-chain branches, RMS = root mean-square radius of gyration,  $g_M$  = branching ratio, all values were determined by GPC-MALLS; Calculations follow Ref. 24.; Standard deviations are reported in parentheses.

The longest alkenylsilane, 7-octenylsilane, produces polyethylenes with approximately 10 total branches + 2.0 LCB per 1000 carbon atoms for both mono- and binuclear systems, respectively (Table 2-7, entries 7-8). As the alkenylsilane chain length increases, the selectivity for comonomer incorporation decreases, reasonably a consequence of differential non-bonded repulsions. It is likely that the smaller alkenylsilanes undergo more facile coordination/insertion<sup>34, 35</sup> in the catalyst coordination sphere due to attenuated steric repulsion from the ancillary ligands, the polymeryl fragment, and the counteranion (e.g., **5**). It is similarly reasonable that longer-chain alkenylsilanes undergo more sluggish coordination/enchainment due to greater steric impediments (e.g., **6**).



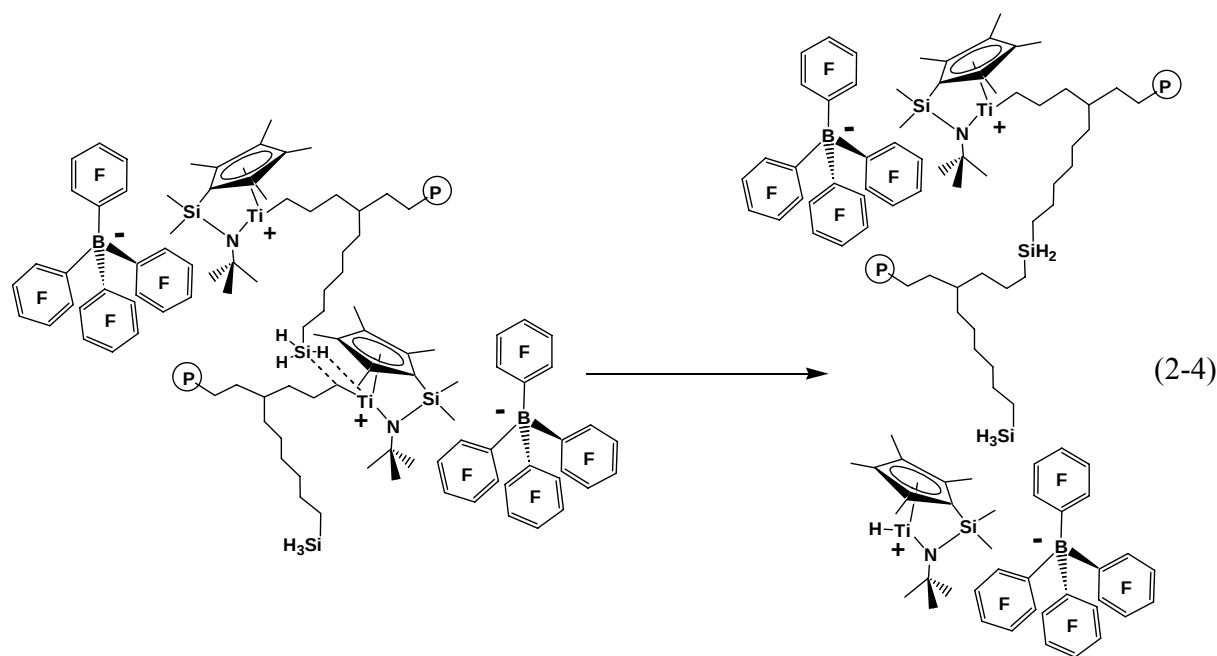
The selectivity for the types of polyolefin branches created during organotitanium-mediated copolymerization of alkenylsilanes with ethylene is largely dependent on alkenylsilane chain dimensions, as assessed by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectroscopy and by GPC-MALLS. In the allylsilane + ethylene system, appreciable densities of short methylsilane branches dominate the copolymer microstructural branching (Figure 2-4). Such branches appear to be too short to chain transfer intermolecularly to other growing polymer chains with very high selectivity (e.g., **7**) to achieve chain coupling, although GPC-MALLS data indicate this is not completely

impossible, simply less efficient compared to longer alkylsilane branches (see below). The two propagating polymer chains must achieve close proximity for a methylsilane branch to realize efficient intermolecular chain transfer to a second propagating polymer chain. These short branches also appear to be too short to effect efficient intramolecular chain transfer due to the enhanced ring-strain associated with this type of “back-biting” (e.g., **8**). The 3-butenylsilane + ethylene and 5-hexenylsilane + ethylene systems produce copolymers with significant densities of ethylsilane and *n*-butylsilane branches, respectively. In addition, these branches are sufficiently long to support extensive intermolecular chain transfer from silyl groups on the



branches. Note that there are prominent signals for secondary silane ( $\text{-SiH}_2\text{-}$ ) groups in the  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra (Figures 2-1, 2-6). In the 7-octenylsilane + ethylene copolymerization system, the long *n*-hexylsilane branches are the shortest branches detected in the polymer microstructure. These *n*-hexylsilane branches are again adequately long to undergo intermolecular chain transfer to a second growing chain with greater efficiencies than methylsilane branches (eq 2-4; Scheme 2-2). Although alkylsilane-branch chain transfer is expected to be considerably less efficient than alkenylsilane-mediated chain transfer, as seen from the aforementioned control experiments with *n*-hexylsilane (Figure 2-3), small but significant amounts of long-chain branching produced by alkylsilane-branch chain transfer

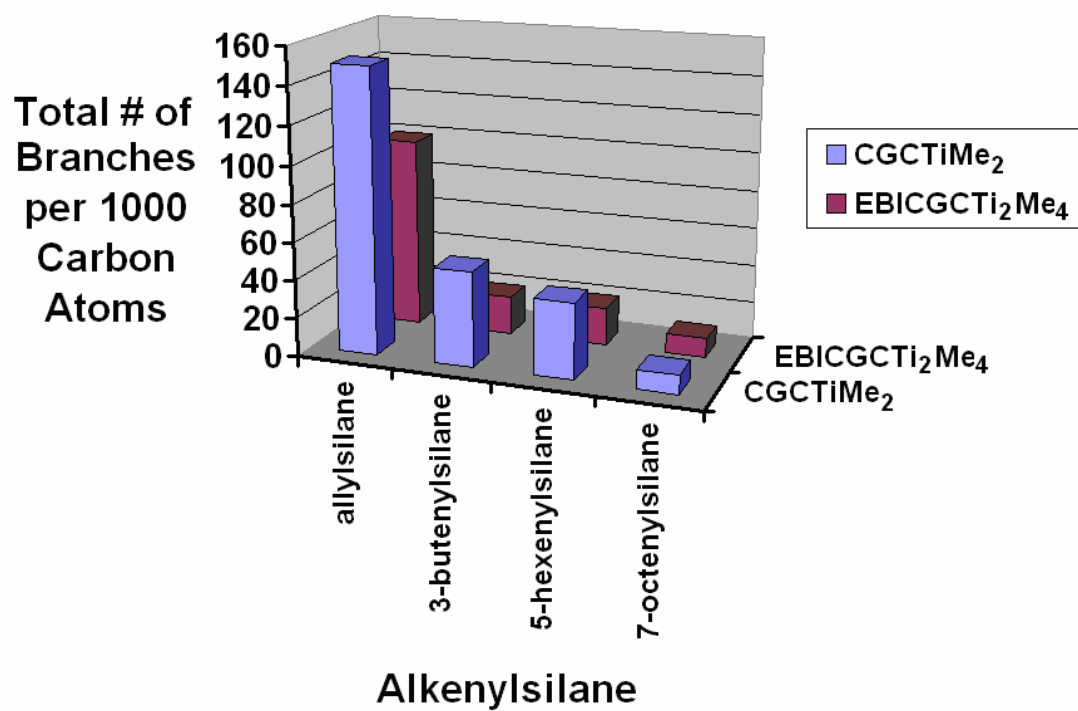
should substantially increase the copolymer molecular weight. In addition, this type of chain transfer may be facilitated for alkenylsilanes of suitable dimensions, by the binuclear Ti catalyst holding two polymer chains in close proximity, although this effect is generally small. Thus, this form of cooperativity may be operative for the binuclear catalyst-mediated allylsilane + ethylene and possibly the 3-butenylsilane + ethylene systems (Table 2-7, entries 2 and 4). The  $^1\text{H}$  NMR spectrum of the 7-octenylsilane + ethylene copolymer exhibits intense resonances for  $-\text{SiH}$ ,  $-\text{SiH}_2$ , and  $-\text{SiH}_3$  moieties, suggesting formation of a variety of pendant groups including long- and short-chain branches (Figure 2-8).



In the aforementioned copolymerization systems, longer branch lengths generally correlate with greater extents of long-chain branching, reflecting the potential kinetic advantage of longer branches to more readily contact a second metal-polymeryl center with minimal steric impediment (e.g., eq 2-4). Considering the total branch density formed during *mononuclear* catalyst-mediated polymerization, 6 % of all branches are LCB in allylsilane + ethylene

copolymers, 20 % of all branches are LCB in 3-butenylsilane + ethylene copolymers, 25 % of all branches are LCB in 5-hexenylsilane + ethylene copolymers, and 20 % of all branches are LCB in 7- octenylsilane + ethylene copolymers. Considering the total branch density formed during *binuclear* catalyst-mediated polymerization, 10 % of all branches are LCB in allylsilane + ethylene copolymers, 25 % of all branches are LCB in 3-butenylsilane and 5-hexenylsilane + ethylene copolymers, and 20 % of all branches are LCB in 7- octenylsilane + ethylene copolymers. These LCB densities reflect the relative efficiency of alkylsilane branches to under intermolecular chain transfer. Furthermore, the shorter the alkenylsilane chain length, the larger the density of short-chain branching due to more facile activation/enchainment in both the mono- and binuclear catalyst systems (Figure 2-10).

**Figure 2-10.** Relationship of the density of short-chain branches to alkenylsilane chain length for CGCTiMe<sub>2</sub>- and EBICGCTi<sub>2</sub>Me<sub>4</sub>-mediated copolymerization of alkenylsilanes with ethylene.



The LCB trends are reflected in the dramatic differences in physical properties of the copolymers mentioned above. As the chain density of LCB increases, the polymer melting temperatures noticeably decrease compared to polyethylene (Tables (2-1)–(2-6)). These trends illustrate the capacity to control the LCB density and tune polyolefin microstructure simply by altering the alkenylsilane chain length. Multi-Angle Laser-Light Scattering (MALLS)-derived branching ratios,  $g_M$ , are found to increase with increasing alkenylsilane chain length and follow the trend:

$$0.1 \approx g_M(C_3) < g_M(C_4) \approx g_M(C_6) < g_M(C_8) \approx 1.0$$

The branching ratio is defined by eq. 2-5,<sup>36</sup> where  $\langle r_g^2 \rangle_{\text{branch}}$  is the root mean-square radius of gyration of the branched polymer and  $\langle r_g^2 \rangle_{\text{linear}}$  is the root mean-square radius of gyration of the corresponding linear polymer of identical molecular weight (Table 2-7). Thus  $g_M$  compares the root mean-square radii of branched and linear macromolecules of equivalent molecular weight,

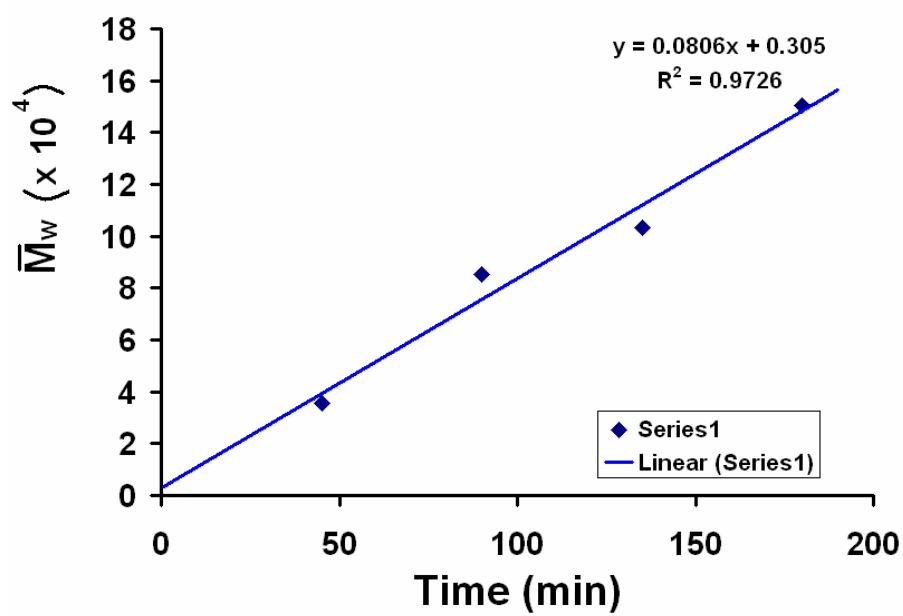
$$g_M = \frac{\langle r_g^2 \rangle_{\text{branch}}}{\langle r_g^2 \rangle_{\text{linear}}} \quad (2-5)$$

and since branched molecules are more compact than the linear analogues,  $g_M$  values can provide relative branch density based on how close the value approaches 0.0 or 1.0. This branching ratio data trend is further evidence for the presence of greater densities of total branches as the alkenylsilane chain length decreases. The branching ratios also indicate that all of the C<sub>3</sub>-C<sub>6</sub> alkenylsilane + ethylene copolymers have considerably smaller radii than the linear analogues, arguing for significant branch formation in all of these copolymerization systems. Furthermore, the significantly smaller total branch density for 7-octenylsilane gives rise to a branching ratio of

approximately 1.0, which is attributable to more sluggish coordination/enchainment due to greater steric impediments.

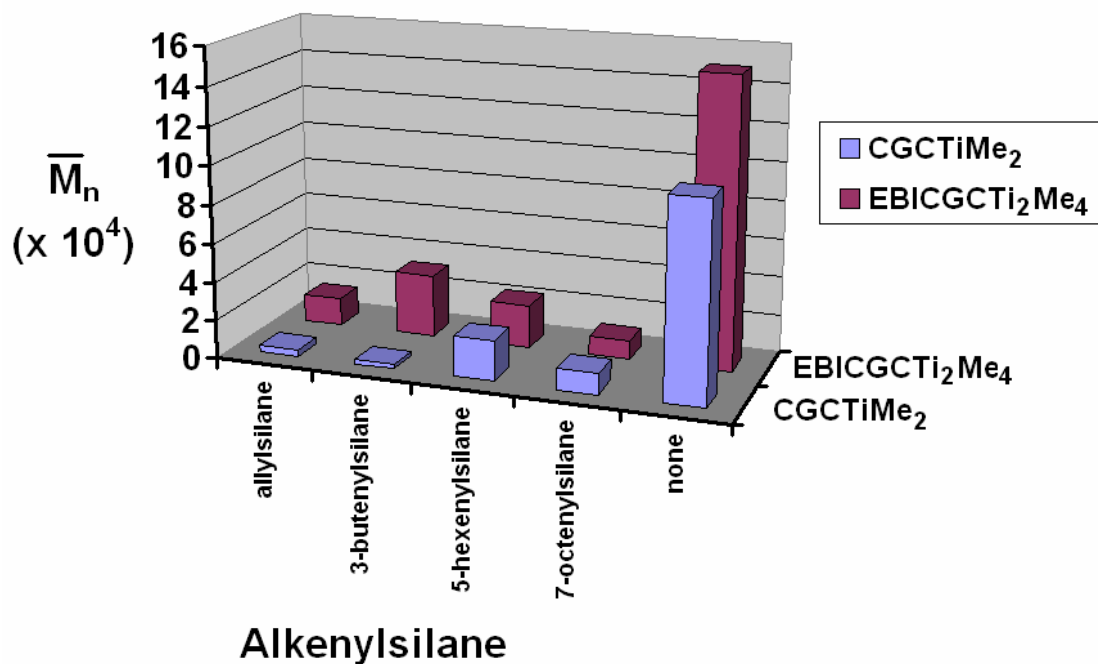
As shown by the GPC-MALLS data for the present copolymerization systems, longer branch lengths generally correlate with larger extents of long-chain branching, reflecting the potential kinetic advantage of longer branches to more easily contact a second metal-polymeryl center with minimal steric impediment (e.g., eq 2-4). For the mononuclear catalyst-mediated 7-octenylsilane + ethylene system, the copolymer molecular weight scales linearly with polymerization time (Figure 2-11). Figure 2-11 indicates that as the polymerization reaction progresses with increasing time, the likelihood of a hexylsilane branch to contact an additional Ti-polymeryl species and effect chain transfer also increases. It is probable that the large increase in copolymer molecular weight is attributable to long-chain branch formation via hexylsilane-branch chain transfer.

**Figure 2-11.** Relationship of the copolymer molecular weight to polymerization time for CGCTiMe<sub>2</sub>-mediated copolymerization of 7-octenylsilane with ethylene.

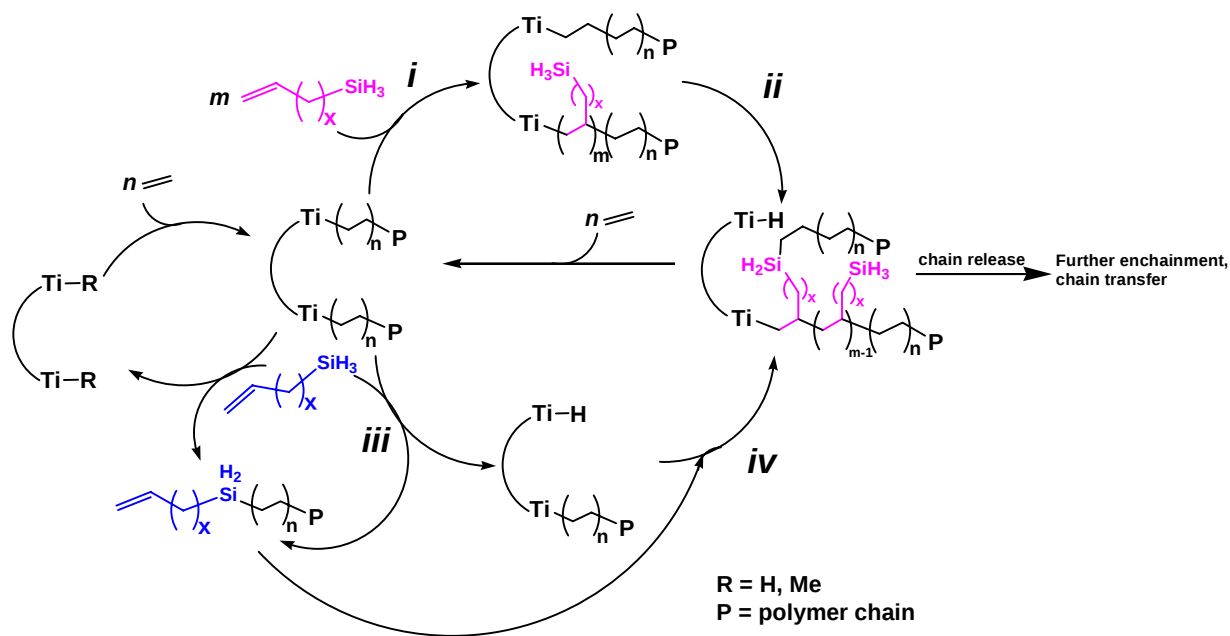


**Alkenylsilane Chain Length Effects on Chain Transfer Efficiency.** In the present organotitanium-mediated alkenylsilane + ethylene copolymerization systems, where a homologous series of alkenylsilanes is employed as chain transfer agents, all alkenylsilanes are found to efficiently effect chain termination. Comparing copolymer  $M_n$  data with alkenylsilane chain length (at identical alkenylsilane concentrations) for both mononuclear and binuclear Ti catalyst systems, copolymer molecular weights are invariably smaller than those of the corresponding ethylene homopolymers produced with identical catalysts (Figure 2-12, Table 2-4). Furthermore, the EBICGCTi<sub>2</sub>Me<sub>4</sub>-mediated polymerization systems consistently produce higher molecular weight polymers than those of the mononuclear catalyst system (albeit with somewhat lower activity and lower comonomer incorporation selectivity). The presence of two Ti centers in close proximity most likely facilitates insertion of a chain-transferred copolymer product (Scheme 2-3, step iv) and/or chain transfer of a growing polymer chain by an alkylsilane branch on another growing polymer chain (Scheme 2-3, step ii). The binuclear Ti system chain transfer plots (Figures 2-13c, d) reveal significant deviations for longer alkenylsilanes, and for shorter alkenylsilanes exhibit slight deviations (Figures 2-13a, b) from the ideal, linear chain transfer plots produced with the mononuclear Ti system (e.g., Figures 2-2a, 2-3a, 2-5a, 2-7a), suggesting some degree of cooperativity between the two active Ti centers in effecting enchainment and chain transfer, depending on the alkenylsilane chain length. A likely explanation for this nonlinear behavior is enhanced interchain and intrachain Si–C coupling processes due to the close proximity of the two Ti centers.

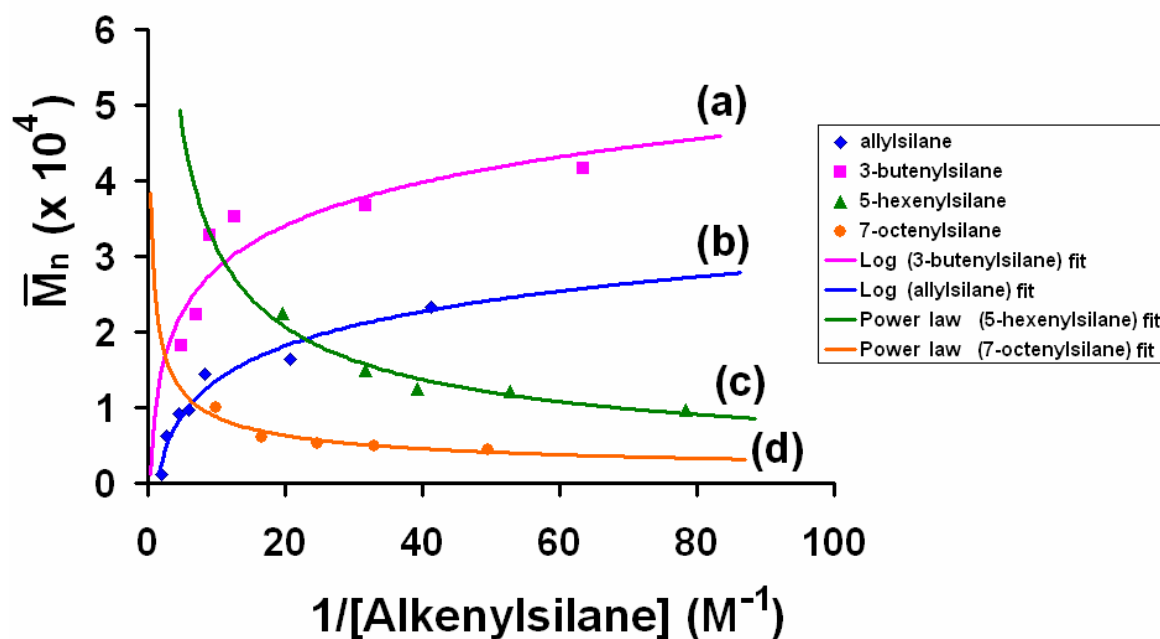
**Figure 2-12.** Dependence of copolymer number-average molecular weight on alkenylsilane chain length at constant 100 mM [alkenylsilane] for CGCTiMe<sub>2</sub>- and EBICGCTi<sub>2</sub>Me<sub>4</sub>-mediated copolymerization of alkenylsilanes with ethylene.



**Scheme 2-3.** Proposed Catalytic Cycle for Binuclear Organotitanium-Mediated Alkenylsilane + Ethylene Copolymerization



**Figure 2-13.** Comparison of ethylene + alkenylsilane copolymer number average molecular weight (GPC vs. polyethylene) relationship to inverse concentrations of : (a) 3-butenylsilane (b) allylsilane (c) 5-hexenylsilane (d) 7-octenylsilane at identical fixed EBICGCTi2Me4 and ethylene concentrations.



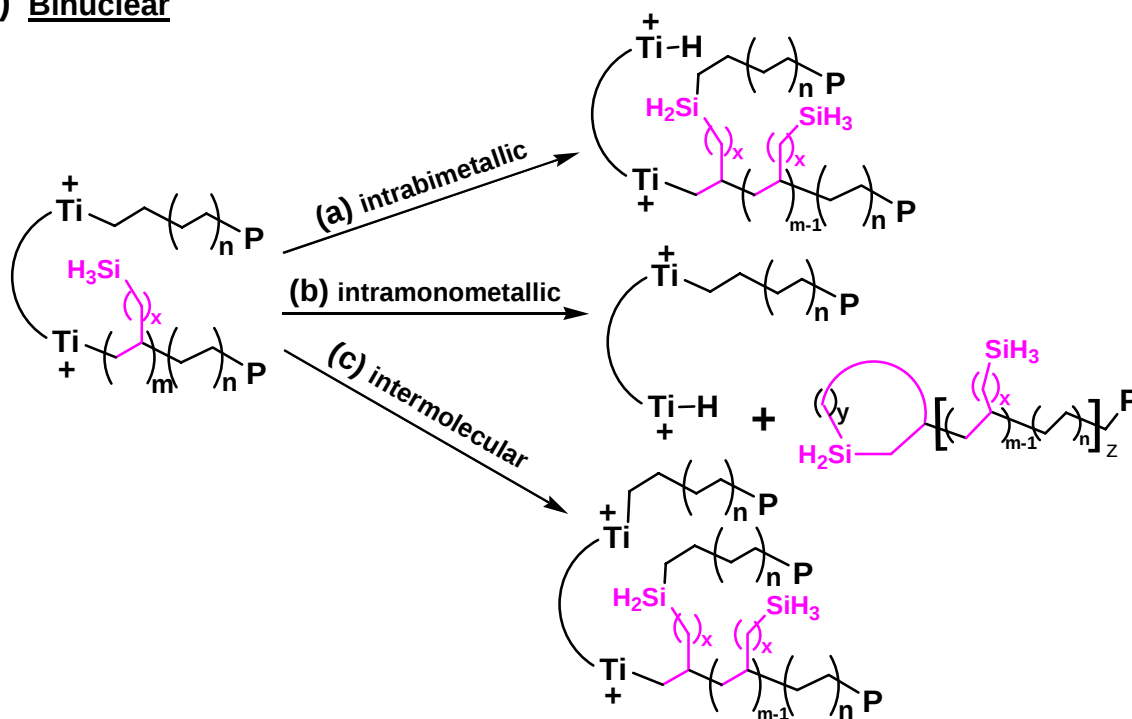
**Ti Nuclearity Effects on Alkenylsilane Chain Transfer.** As noted above, binuclear Ti catalyst EBICGCTi<sub>2</sub>Me<sub>4</sub> consistently produces higher molecular weight polyolefins than does the mononuclear CGCTiMe<sub>2</sub> analogue. A reasonable explanation invokes a cooperative enchainment/chain transfer process involving the two proximate active centers, resulting in more probable macromonomer reinsertion or alkylsilane-branch chain transfer to a growing chain (Scheme 2-3, steps iv and ii, respectively). In regard to enchainment selectivity, this type of olefin insertion cooperativity between two proximate Ti centers has been previously shown to afford high molecular weight polyolefins with noticeably enhanced  $\alpha$ -olefin comonomer incorporation versus the mononuclear analogue.<sup>12</sup> Previously, it was proposed that the dicationic bimetallic framework likely displays enhanced  $\alpha$ -olefin binding affinity/kinetic detainment (e.g., **3**) leading to increased comonomer enchainment.<sup>12</sup> Bimetallic cooperative effects resulting in such reaction sequences (Scheme 2-3) here would generate higher molecular weight polyolefin products with long-chain branching as a consequence of the longer comonomer-derived –SiH<sub>3</sub>–terminated branches in the polymer microstructure. Note that this intradimer silanolytic chain transfer process as a means to introduce long-chain branching is unprecedented. Intriguingly, the present binuclear Ti catalyst mediates alkenylsilane chain transfer in dramatically different ways, depending on the alkenylsilane chain length. For short alkenylsilanes (C<sub>3</sub> and C<sub>4</sub>) with the bimetallic catalyst, the chain transfer plots indicate an approximate logarithmic relationship in which polymer molecular weight falls sublinearly with increasing alkenylsilane concentration (Figures 2-5b and 2-7b, respectively). A plausible explanation is that at low alkenylsilane concentrations, the lower levels of comonomer enchainment adequately depress the effective local silane concentration and thus the chain

transfer rate, as to produce polymers of only modestly varying molecular weights.<sup>37</sup> In addition, at high alkenylsilane concentrations, greater comonomer enchainment increases the effective local silane concentration nonlinearly to enhance intrabimetallic or monometallic chain transfer (Scheme 2-4, pathway **I**, eqs (a) and (b), respectively). These types of interactions<sup>38</sup> between Ti centers and the weakly basic, enchainment  $-\text{SiH}_3$  groups may also block olefin activation, thus depressing propagation rates and causing polymer molecular weight to fall sublinearly with increasing alkenylsilane concentration via Scheme 2-4, pathway **I**.

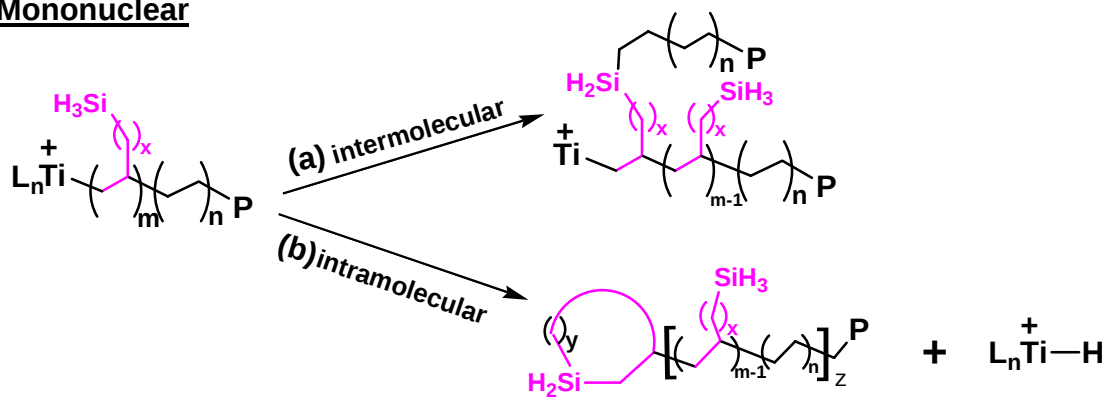
In contrast to the shorter alkenylsilanes, chain transfer plots involving longer alkenylsilanes ( $\text{C}_6$  and  $\text{C}_8$ ) exhibit a power series relationship in which polymer molecular weight increases superlinearly with increasing alkenylsilane concentration (Figures 2-2b and 2-9b, respectively). This superlinear relationship correlates with an increase in the proportion of long-chain branches produced in the corresponding copolymer microstructures (Table 2-7). Interestingly, only in the case of 7-octenylsilane does the mononuclear Ti system also demonstrate a superlinear power series chain transfer relationship. A plausible explanation for these observations is that the longer  $\omega\text{-SiH}_3$  branches, formed by enchainment of these  $\text{C}_6$  and  $\text{C}_8$  alkenylsilanes, can readily chain transfer to growing polymer chains in an intradimer/cooperative manner (Scheme 2-4, pathway **I**, eq (a)) or, for the mononuclear catalyst, via an intermolecular process (Scheme 2-4, pathway **II**, eq (a)). The longer branches maximize the probability at which chain transfer can occur between two polymer chains and thus enhance the selectivity for alkylsilane-branch chain transfer (Scheme 2-4, pathway **I**, eq (a)-(c); eq 2-4). This chain transfer process is supported by the 1: 1: 2  $^1\text{H}$  NMR integration seen for  $-\text{SiH}_3$ :  $>\text{SiH}_2$ :  $>\text{SiH}-$  groups in Figure 2-8. Such cooperativity effects combined with longer branches

**Scheme 2-4.** Chain transfer pathways for (I) Binuclear Ti-mediated silane chain transfer and (II) Mononuclear-mediated silane chain transfer.

**(I) Binuclear**

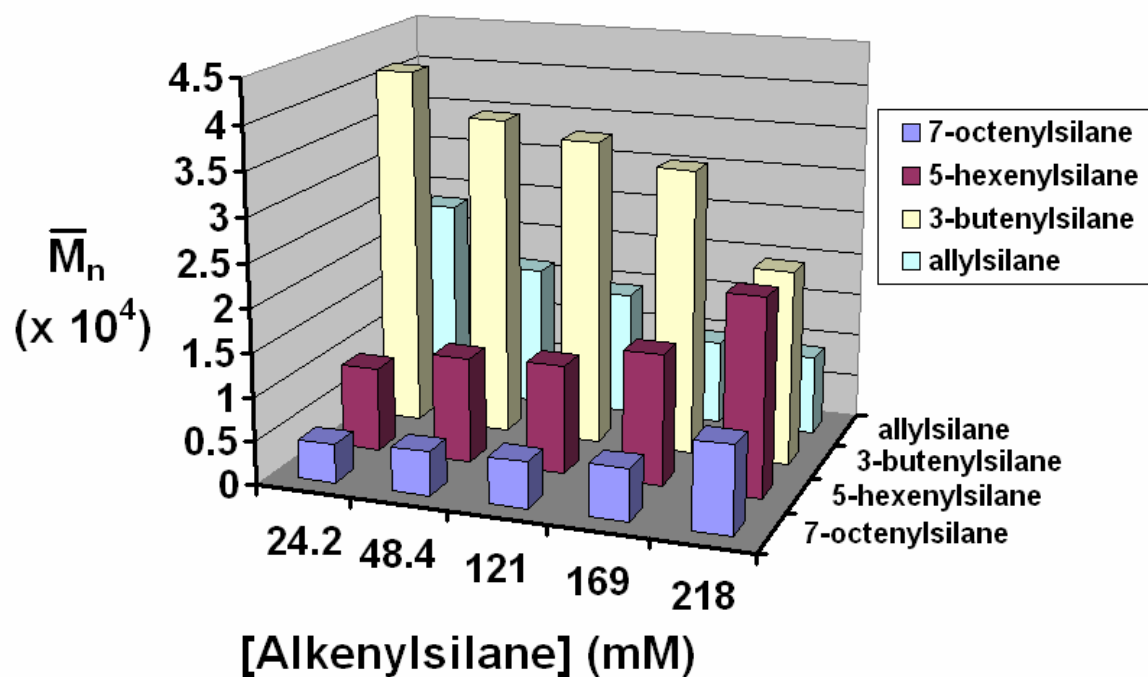


**(II) Mononuclear**



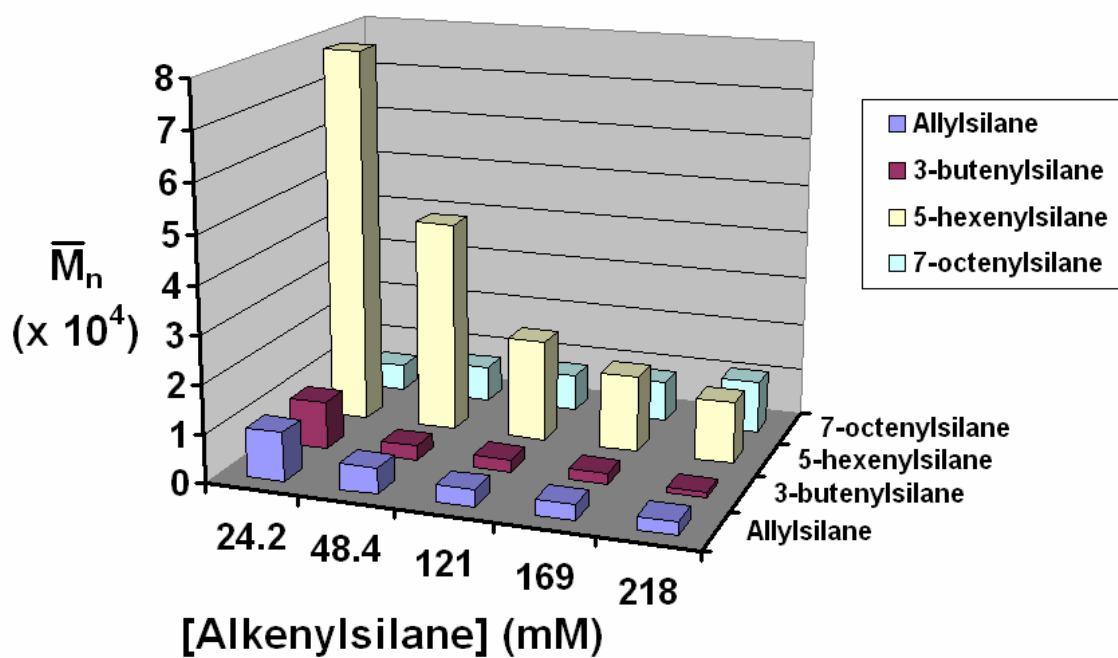
would result in superlinearly increased polymer molecular weight with increasing alkenylsilane concentrations. In addition, even without this type of cooperativity, the longer  $\omega$ -SiH<sub>3</sub> branches would also have the capability of effecting intramolecular silanolytic chain transfer to produce cyclized chain ends (Scheme 2-4, pathway **I**, eq (b)). At low alkenylsilane concentrations, less comonomer is incorporated, thus minimizing the local effective density of alkylsilane branches available to undergo intradimer chain transfer, thereby producing lower molecular weight polymer. This binuclear cooperativity in combination with alkenylsilane chain length effects accounts for the opposite chain transfer trends observed for short versus long alkenylsilanes (Figures 2-13, 2-14).

**Figure 2-14.** Dependence of copolymer  $\bar{M}_n$  on alkenylsilane chain length and concentration for EBICGCTi<sub>2</sub>Me<sub>4</sub>-mediated copolymerization of alkenylsilanes with ethylene.

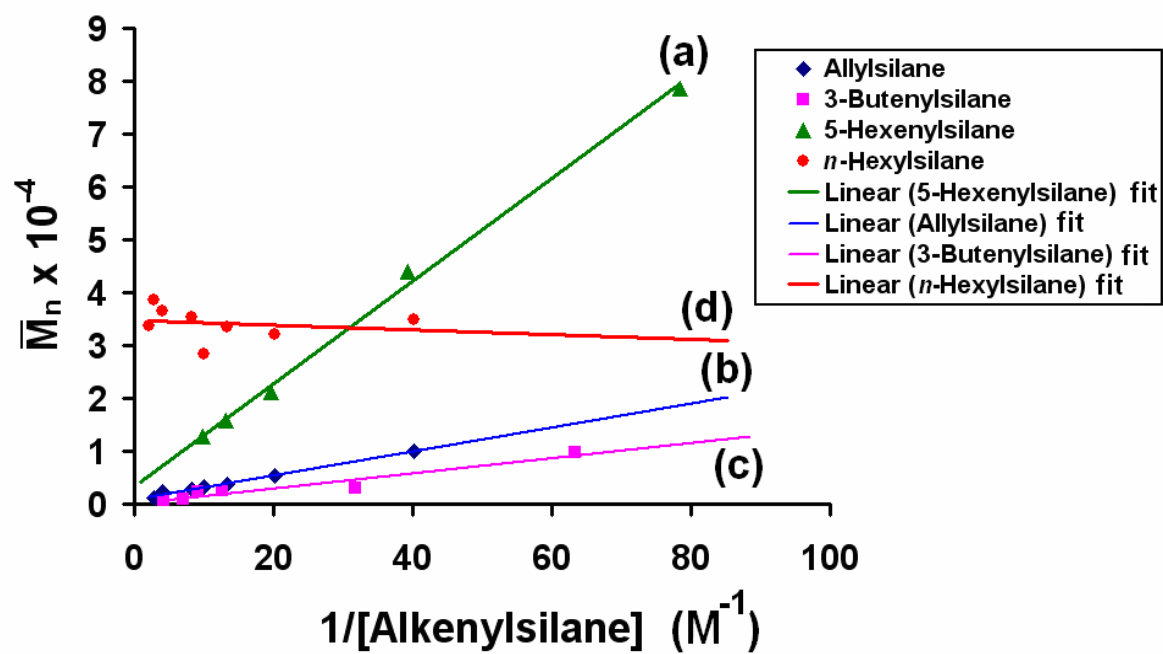


The mononuclear CGCTiMe<sub>2</sub>-catalyzed copolymerization systems exhibit ideal chain transfer behavior for alkenylsilanes ranging from C<sub>3</sub> to C<sub>6</sub> (Figures 2-15, 2-16). In these systems, polymer molecular weight decreases linearly with increasing alkenylsilane concentration. In contrast, with increasing *n*-hexylsilane concentration, the number average molecular weight of the polyethylene product does not decrease linearly, indicating that the olefinic moiety is essential for efficiency in the alkenylsilane chain transfer process. The data in Figure 2-16 indicate that 3-butenylsilane has the greatest chain transfer efficiency, likely due to its moderate size. Allylsilane is sufficiently small to be sterically competitive with ethylene insertion, and thus allylsilane propagation is more rapid than silane chain transfer. In addition, Figure 2-16 shows that 5-hexenylsilane is sufficiently encumbered to exhibit depressed insertion rates vs. chain transfer rates in comparison with the smaller alkenylsilanes. Alkenylsilanes ranging from C<sub>3</sub> to C<sub>6</sub> exhibit very efficient, ideal chain transfer pathways in support of the predominance of Scheme 2-2. In marked contrast, longer 7-octenylsilane deviates significantly from this ideal behavior (Figure 2-9a). The chain transfer behavior in the mononuclear CGCTiMe<sub>2</sub>-mediated system for 7-octenylsilane/ethylene copolymerization is similar to that in the aforementioned binuclear systems, with polymer molecular weights scaling as a power series with increasing alkenylsilane concentration (Figure 2-9). This comonomer creates long hexylsilane branches when enchainment, likely resulting in higher molecular weight polymers at high silane concentrations due to intermolecular alkylsilane-branch chain transfer to other growing polymer chains (eq 2-4). At lower 7-octenylsilane concentrations, the aforementioned chain transfer is less probable due to lower levels of comonomer enchainment, thus resulting in lower molecular weight copolymer. At relatively short alkenylsilane chain lengths (C<sub>3</sub> to C<sub>6</sub>),

**Figure 2-15.** Dependence of copolymer  $M_n$  on alkenylsilane chain length and concentration for CGCTiMe<sub>2</sub>-mediated copolymerization of alkenylsilane with ethylene.



**Figure 2-16.** Comparison of ethylene + alkenylsilane copolymer number-average molecular weight (GPC vs. polyethylene) relationship to inverse concentrations of : (a) 5-hexenylsilane (b) allylsilane (c) 3-butenylsilane (d) *n*-hexylsilane at identical fixed CGCTiMe<sub>2</sub> and ethylene concentrations.



alkenylsilane chain transfer behavior is nearly ideal as seen in Figure 2-16, whereas at longer chain lengths ( $C_8$ ), alkenylsilane chain transfer behavior is still efficient, but deviates from ideality (Figure 2-9a), suggesting that LCB content in the polymer microstructure can be tuned by varying catalyst nuclearity as well as alkenylsilane chain length.

**Kinetics and Mechanism of Organotitanium-Mediated Alkenylsilane + Ethylene Copolymerizations.** A series of polymerizations with varying alkenylsilane concentrations (in pseudo-zero-order excess) was conducted using activated CGCTiMe<sub>2</sub> as the catalyst and with constant catalyst and ethylene concentrations. As noted above, a linear relationship between  $M_n$  and  $1/[\text{alkenylsilane}]$  is observed (Figure 2-16) for alkenylsilanes ranging from  $C_3$  to  $C_6$ , consistent with alkenylsilane acting as the dominant chain transfer agent in an intermolecular process. As noted above, the absence of vinyl resonances and the presence of  $-\text{SiH}_2$  resonances in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra also implicate silanolysis as the dominant chain termination pathway.

Under steady-state conditions, the number average degree of polymerization,  $P_n$ , is equal to the sum of all rates of propagation,  $\sum R_p$ , divided by the sum of the rates of all competing chain transfer pathways,  $\sum R_t$  (eq 2-6).<sup>21</sup> Assuming a single dominant chain transfer process by alkenylsilane and rapid chain reinitiation after chain transfer,  $P_n$  is given by eq 2-7, where  $k_p$  is the rate constant for propagation and  $k_{Si}$  the rate constant for inter/intramolecular silanolytic chain transfer. With polymerizations carried out at constant catalyst and monomer concentration

$$\overline{P}_n = \frac{\sum R_p}{\sum R_t} \quad (2-6)$$

$$\overline{P}_n = \frac{k_p^{ethylene} [ethylene] + k_p^{alkenylsilane} [alkenylsilane]}{k_{Si}^{inter}[alkenylsilane] + k_{Si}^{intra} [alkenylsilane]} \quad (2-7)$$

and with a pseudo-zero-order excess of alkenylsilane, Figure 2-16 shows that eq 2-7<sup>4a</sup> is obeyed over a broad silane concentration range (except for 7-octenylsilane).<sup>21, 25, 39</sup> Using this equation and the data in Figure 2-16b yields rate constant ratios for mononuclear Ti-mediated copolymerizations (Table 2-8). The  $k_p^{alkenylsilane}/k_{Si}^{total}$  rate constant ratios are all  $\geq 1$  and argue that chain transfer predominantly occurs subsequent to alkenylsilane enchainment. The alkenylsilane rate of insertion must be greater than the rate of total silane chain transfer to result in ratios  $\geq 1$ , thus arguing that alkenylsilane enchainment occurs before the process of silane chain transfer. This explanation is in excellent agreement with the arguments advanced above to explain deviations from linearity in  $M_n$  vs.  $[alkenylsilane]^{-1}$  plots and the large LCB yields. In addition, as the alkenylsilane chain length decreases, the rate of alkenylsilane propagation becomes more competitive with ethylene propagation, doubtless reflecting steric factors.

**Table 2-8.** Kinetic Rate Constant Ratios for CGCTiMe<sub>2</sub>—Catalyzed Copolymerization

| Entry | Ratio <sup>a</sup>                   | allylsilane | 3-butenylsilane | 5-hexenylsilane |
|-------|--------------------------------------|-------------|-----------------|-----------------|
| 1     | $k_p^{alkenylsilane}/k_{Si}^{total}$ | 20          | 1               | 5               |
| 2     | $k_p^{ethylene}/k_{Si}^{total}$      | 40          | 30              | 180             |

<sup>a</sup>Rate constant ratios were calculated from  $M_n$  vs.  $1/[alkenylsilane]$  plots using the following equation:

$$\overline{P}_n = \frac{k_p^{ethylene} [ethylene] + k_p^{alkenylsilane} [alkenylsilane]}{k_{Si}^{inter} [alkenylsilane] + k_{Si}^{intra} [alkenylsilane]}$$

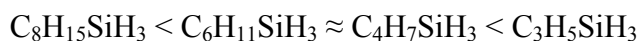
Further evaluation of the role of the silane C=C functionality in the chain transfer process was carried out with control polymerizations using saturated *n*-hexylsilane as the chain transfer agent.  $^1\text{H}$  NMR integration of  $\text{SiH}_2$  versus vinyl resonances indicates the formation of predominantly vinyl-terminated polyethylenes, consistent with literature support for  $\beta$ -H elimination as the predominant chain transfer process in ethylene +  $\alpha$ -olefin copolymerization processes with these catalysts.<sup>4b</sup> Furthermore, the plot of  $M_n$  vs.  $1/[\textit{n}\text{-hexylsilane}]$  reflects non-ideal chain transfer with the near-zero slope indicating that  $k_{\text{Si}}/k_p \approx 0$  (Figure 2-16d), and that silanolytic chain transfer is not the dominant termination pathway. In fact, alkenylsilanes are far more efficient chain transfer agents than are alkylsilanes ( $k_p^{\text{ethylene}}/k_{\text{Si}}^{\text{total}}$  for *n*-hexylsilane is up to 150 x greater than that of alkenylsilanes), indicating that the olefinic moiety is essential in alkenylsilane chain transfer. An appealing explanation is that the alkenylsilane chain transfer rates are enhanced by high effective local silane concentrations achieved in proximity to the electrophilic Ti center where the silyl group is held proximate to the Ti center either by insertion into the growing polymer chain (as argued above) or by interaction of the weakly basic silyl group with the Ti center<sup>4c, d, 17, 40</sup> (presumably via Scheme 2-2, step iii, iv; less likely on the basis of the *n*-hexylsilane results). In addition, the olefinic moiety in the alkenylsilane may play a role by interacting with the electrophilic Ti center via olefin  $\pi$ -coordination,<sup>28</sup> also resulting in high effective local silane concentrations proximate to the active site.

CGCTiMe<sub>2</sub>-mediated ethylene + 7-octenylsilane copolymerizations were conducted (Table 2-6, entries 1-7) with constant catalyst and monomer concentrations over a wide range of 7-octenylsilane concentrations (all in pseudo-zero-order excess). Interestingly, a superlinear relationship is observed between  $M_n$  and  $1/[\text{7-octenylsilane}]$  (Figure 2-9) suggesting that the

alkenylsilane length allows additional macromolecule-building chain transfer processes beyond the conventional intermolecular Ti-polymeryl scission process (Scheme 2-3). Similarly, polymerizations with varying alkenylsilane concentrations (in pseudo-zero-order excess) were conducted using  $\text{EBICGCTi}_2\text{Me}_4$  as the catalyst. That a sublinear relationship between  $M_n$  and  $1/[\text{alkenylsilane}]$  is observed (Figures 2-5b and 2-7b) for alkenylsilanes ranging from  $\text{C}_3$  to  $\text{C}_4$ , is consistent with the alkenylsilane acting as the dominant chain transfer agent both inter- and intramolecularly at high  $[\text{alkenylsilane}]$ . In these systems, the LCB content compared to the total number of branches is approximately 10 % and 20 %, respectively, supporting the presence of both the inter- and intramolecular chain transfer processes. Unlike the shorter alkenylsilanes, a superlinear relationship between  $M_n$  and  $1/[\text{alkenylsilane}]$  is observed (Figures 2-2b and 2-9b) for alkenylsilanes of chain length  $\text{C}_6$  and  $\text{C}_8$ . Here, high alkenylsilane concentrations produce high molecular weight polymer, most likely due to enhanced selectivity of presumably intradimer alkylsilane-branch chain transfer/macromolecule growing processes resulting in longer-chain branches (Scheme 2-3, step ii). In these systems, the LCB content compared to total number of branches is 25 % and 20 %, respectively, supporting the presence of the aforementioned chain transfer/macromolecule growing processes. These nonlinear systems are too kinetically complex to analyze using eqs 2-6 and 2-7, mentioned above. In these nonlinear cases, multiple chain transfer processes (Scheme 2-4) appear to be operative, including intermolecular transfer by alkenylsilane, intermolecular transfer by macromonomer silyl-branches, intradimer transfer by silyl-branches, and intramolecular cyclization by silyl-branches. These silanolytic chain transfer processes are far too multifaceted to be analytically tractable.

## Conclusions

This investigation demonstrates that alkenylsilanes are versatile single-site comonomers having both the kinetic competence to efficiently effect silanolytic chain transfer in a variety of environments as well as the ability to undergo rapid insertive chain propagation. Moreover, the overall effectiveness of propagation for organotitanium-mediated copolymerizations with ethylene follows the order:



Smaller alkenylsilanes have more competitive propagation rates vs. ethylene as demonstrated by the large densities of short-chain branching in these systems. Longer alkenylsilanes have less competitive propagation rates compared to ethylene, however the resulting polymers possess longer branches which subsequently undergo silanolytic chain transfer to other growing polymer chains, thus enhancing selectivity for long-chain branching. Furthermore, as the polymerization reaction time increases, the copolymer molecular weight linearly increases, suggesting long-chain branch formation via silane-branch chain transfer. Among the alkenylsilanes, 3-butenylsilane is the most efficient chain transfer agent for CGCTiMe<sub>2</sub>-mediated systems as a consequence of its moderate size. In addition, longer 7-octenylsilane is the most efficient chain transfer agent for EBICGCTi<sub>2</sub>Me<sub>4</sub>-mediated copolymerizations as a consequence of its potential to contact other Ti-polymeryl moieties as well as to undergo facile intramolecular chain transfer with minimum ring-strain in the resulting products. Allylsilane and 5-hexenylsilane are also found to be efficient chain transfer agents for organotitanium-mediated polymerizations and produce substantial amounts of long-chain branching.

Several series of CGCTiMe<sub>2</sub>-mediated polymerizations with varying alkenylsilane concentrations were examined and found to exhibit high polymerization activities, high product molecular weights,  $M_w/M_n \approx 2.0$ , negligible competing  $\beta$ -H elimination, and with a linear relationship between  $M_n$  and  $1/[\text{alkenylsilane}]$ , all of which are consistent with a dominant silanolytic chain termination mechanism. Although the EBICGCTi<sub>2</sub>Me<sub>4</sub>-mediated polymerizations exhibit nonlinear relationships between  $M_n$  and  $1/[\text{alkenylsilane}]$ , these systems also exhibit high polymerization activities, high product molecular weights,  $M_w/M_n \approx 2.0$ , and negligible competing  $\beta$ -H elimination, consistent with a dominant, silanolytic chain termination mechanism. The ability to tune and modify the polyolefin microstructure (functional groups, long-chain branching) by varying the alkenylsilane chain length confers a great deal of flexibility on these polymerization systems. The versatility of these systems suggests the possibility of new and useful multi-purpose comonomers for controlling polymer microstructure.

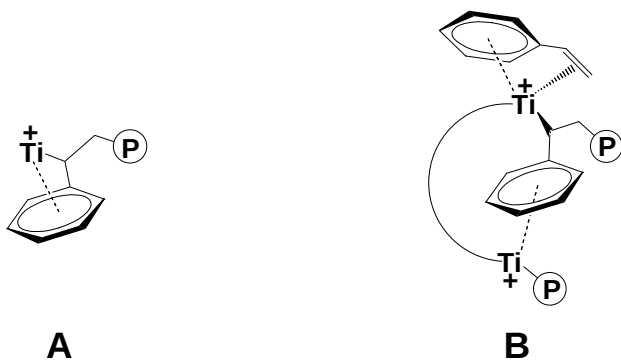
We have shown here that organotitanium-mediated silanolytic chain transfer and ethylene +  $\alpha$ -olefin copolymerization can be coupled in a catalytic cycle to produce silane-terminated, highly branched copolymers with high propagation activities and narrow product molecular weight distributions. Therefore, introduction of alkenylsilanes into organotitanium-mediated ethylene polymerization systems is a versatile, effective new way of incorporating branches of various lengths and functionality into an otherwise inert polymer.

## **CHAPTER 3**

Organosilane Effects on Organotitanium-Catalyzed Styrene Polymerization

## Introduction

Polystyrenes have a range of useful applications including anticorrosion coatings, thermoplastics, and foams.<sup>1</sup> Over the past decade, techniques to produce, control, and understand single-site styrene polymerization processes have been widely explored.<sup>2</sup> Although many advances have been made in understanding the polymerization mechanism, only a relatively restricted class of catalysts is known to efficiently polymerize styrene.<sup>3</sup> While Cp'TiXYZ-derived catalysts (Cp' = substituted or unsubstituted cyclopentadienyl; X, Y, Z = Cl, alkyl, alkoxy, etc. ligand) are among the most effective,<sup>4</sup> the active species are not well-defined and there is debate concerning how many and what the active species may be.<sup>5</sup> In contrast, *ansa*-amido monocyclopentadienyl Ti constrained geometry catalysts (CGCs) are known to be virtually inactive for styrene homopolymerization.<sup>6</sup> It is thought that this inertness is a consequence of catalyst inactivation/binding by the phenyl ring  $\pi$ -system of a 2,1-inserted monomer unit (e.g., **A**).<sup>6</sup> Previous work from this laboratory showed that increasing the CGC catalyst nuclearity can significantly overcome these constraints by a process that is thought to involve preferential binding of the last inserted (deactivating) styrene to the adjacent Ti-center (e.g., **B**).<sup>7</sup> These observations raise the intriguing question of whether a similar polymerization



rate effect could be achieved via addition of a weakly basic reagent instead of altering the catalyst nuclearity to weaken the  $\pi$ -complexation. We report here that alkenyl-, aryl-, and alkylsilane addition to mononuclear CGCTiMe<sub>2</sub>-mediated polymerization processes results in very large activity increases for styrene homopolymerization.

## Experimental Section

**Materials and Methods.** All manipulations of air-sensitive materials were carried out with rigorous exclusion of oxygen and moisture in flame- or oven-dried Schlenk-type glassware on a dual-manifold Schlenk line, or interfaced to a high-vacuum line ( $10^{-6}$  Torr), or in a nitrogen-filled MBraun glovebox with a high capacity recirculator ( $< 1$  ppm of O<sub>2</sub>). Argon and ethylene (Matheson, prepurified) were purified by passage through a MnO oxygen-removal column and a Davison 4A molecular sieve column. Hydrocarbon solvents (*n*-pentane and toluene) were dried using activated alumina columns according to the method described by Grubbs,<sup>8</sup> and were additionally vacuum-transferred from Na/K alloy immediately before vacuum line manipulations. All organic starting materials, including chlorosilane starting materials, were purchased from Aldrich Chemical Co. or Strem Chemicals, Inc. and were used without further purification unless otherwise stated. Styrene was stirred over CaH<sub>2</sub> for 5 days and distilled prior to use. Allyltrichlorosilane was purchased from Acros Organics N.V. The solvent, 1,2-difluorobenzene was stirred over CaH<sub>2</sub> for 5 days, distilled, and stored over Davison 4A molecular sieves prior to use. Benzene-d<sub>6</sub>, toluene-d<sub>8</sub>, and 1,1,2,2-tetrachloroethane-d<sub>2</sub> were purchased from Cambridge Isotope Laboratories. The organotitanium precatalysts

$\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}^t\text{Bu})\text{TiMe}_2$ <sup>9</sup> and  $(\text{C}_5\text{Me}_5)\text{TiMe}_3$ <sup>10</sup> were prepared by published procedures. The precatalyst  $(\mu\text{-CH}_2\text{CH}_2\text{-3,3'})\{(\eta^5\text{-indenyl})[1\text{-Me}_2\text{Si}(\text{tBuN})](\text{TiMe}_2)]_2$  was prepared by the published procedure<sup>11</sup> and activated in 1,2-difluorobenzene. The cocatalyst  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  was prepared by the published procedure.<sup>12</sup> All hydrosilane chain transfer agents (e.g., *n*-hexylsilane) were synthesized from corresponding trichlorosilanes (e.g., *n*-hexyltrichlorosilane) according to the literature procedure,<sup>8</sup> stirred over  $\text{LiAlH}_4$  for 48 h, and distilled prior to use. The comonomer allylsilane was synthesized from allyltrichlorosilane according to the literature procedure,<sup>8</sup> stirred over  $\text{LiAlH}_4$  for 48 h, and distilled prior to use. The comonomers 3-butenylsilane, 5-hexenylsilane, and 7-octenylsilane were synthesized in three steps according to modified literature procedures<sup>13, 14, 15</sup>, stirred over  $\text{LiAlH}_4$  for 48 h, and distilled prior to use.

**Physical and Analytical Measurements.** NMR spectra were recorded on either a Varian Mercury- or Inova-400 (FT, 400 MHz,  $^1\text{H}$ ; 100 MHz,  $^{13}\text{C}$ ) or Inova-500 (FT, 500 MHz,  $^1\text{H}$ ; 125 MHz,  $^{13}\text{C}$ ) instrument. Chemical shifts ( $\delta$ ) for  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  are referenced to internal solvent resonances and reported relative to  $\text{SiMe}_4$ . For polymer NMR characterization, 50-100 mg samples were dissolved in 0.5-0.7 mL of  $\text{C}_2\text{D}_2\text{Cl}_4$  (Cambridge Isotope Laboratories) in a 5 mL NMR tube by heating the solution in a 120 °C oil bath. Melting temperatures of polymers were measured by DSC (DSC 2920, TA Instruments, Inc.) from the second scan with a heating rate of 20 °C/min. GPC analyses of polymer samples were performed on a Waters Alliance GPCV 2000 (3 columns, Waters Styragel HT 6E, HT 4, HT 2; operation temperature, 150 °C; mobile phase, 1,2,4-trichlorobenzene; flow rate, 1 mL/min) and are reported relative to 12 polystyrene standards ( $M_w$ = 770, 2430, 3680, 13200, 18700, 29300, 44000, 114200, 212400, 382100, 560900, 891000) purchased from Aldrich Chemical Co. GPC analyses of polymer

samples were also performed on a Polymer Laboratories PL-GPC 220 instrument using 1,2,4-trichlorobenzene solvent (stabilized with 125 ppm BHT) at 150 °C using three PLgel 10  $\mu$ m mixed columns. GC-MS analyses were performed on a HP 6890 instrument equipped with a Zebron ZB-5 dimethylpolysiloxane column (30 m x 250  $\mu$ m x 0.25  $\mu$ m) interfaced to a HP 6890 mass-selective detector. Elemental analysis was performed by the Microanalysis Laboratory at the University of Illinois, Urbana-Champaign.

**Copolymerization of Styrene and 5-Hexenylsilane. Representative Experiment.** In the glove box, a three-necked Morton flask, which had been dried overnight at 160 °C, equipped with a large stir bar and thermocouple, was charged with dry toluene (50 mL). The flask was next attached to a high vacuum line and the toluene was freeze-thaw degassed. Styrene (10.0 mL) was then vacuum-transferred into the flask immediately prior to polymerization, followed by introduction of argon (1.0 atm) with rapid stirring. Next, 5-hexenylsilane (6.0 mmol) was injected into the reactor with rapid stirring and positive Ar pressure. In the glovebox, a 5 mL sample vial equipped with a septum cap was charged with 3.2 mg (0.01 mmol) of  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}^t\text{Bu})\text{TiMe}_2$  and 9.22 mg (0.01 mmol)  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ . A measured amount of toluene (4 mL) was then syringed into the vial with a dry,  $\text{N}_2$ -purged gastight syringe. The vial was shaken for several min, the contents taken up into the syringe, and then removed from the glovebox immediately prior to the polymerization experiment. The catalyst solution was next rapidly syringed through the septum-sealed sidearm into the rapidly stirring reaction flask. After 60 min, methanol (5 mL) was injected to quench the reaction. Excess methanol (~ 500 mL) was then used to precipitate the polymer. The polymer (0.55 g) was collected by filtration, washed with methanol (200 mL), and dried in vacuo at 60 °C for 48 h.

**Polymerization of Styrene in the Presence of *n*-Hexylsilane. Representative Experiment.** In the glove box, a three-necked Morton flask, which had been dried overnight at 160 °C, equipped with a large stir bar and thermocouple, was charged with dry toluene (50 mL). The flask was next attached to a high vacuum line and the toluene was freeze-thaw degassed. Styrene (10.0 mL) was then vacuum-transferred into the flask immediately prior to polymerization, followed by introduction of argon (1.0 atm) with rapid stirring. Next, *n*-hexylsilane (6.0 mmol) was injected into the reactor with rapid stirring and positive Ar pressure. In the glovebox, a 5 mL sample vial equipped with a septum cap was charged with 3.2 mg (0.01 mmol) of  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}^t\text{Bu})\text{TiMe}_2$  and 9.22 mg (0.01 mmol)  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ . A measured amount of toluene (4 mL) was then syringed into the vial with a dry,  $\text{N}_2$ -purged gastight syringe. The vial was shaken for several min, the contents taken up into the syringe, and then removed from the glovebox immediately prior to the polymerization experiment. The catalyst solution was next rapidly syringed through the septum-sealed sidearm into the rapidly stirring reaction flask. After 60 min, methanol (5 mL) was injected to quench the reaction. Excess methanol (~500 mL) was then used to precipitate the polymer. The polymer (0.51 g) was collected by filtration, washed with methanol (200 mL), and dried in vacuo at 60 °C for 48 h.

## Results and Discussion

All polymerizations were carried out under rigorously anhydrous/anaerobic conditions using procedures minimizing mass transport effects,<sup>16</sup> with pseudo-zero-order [styrene] and [organosilane]. Polymeric products were characterized by  $^1\text{H}/^{13}\text{C}$  NMR, GPC, and DSC; data are compiled in Tables 3-1 and 3-2. The results of the CGCTiMe<sub>2</sub>-mediated styrene homopolymerization experiments (Table 3-1) reveal a dramatic increase in polymerization activity upon organosilane addition. Under identical conditions, CGCTiMe<sub>2</sub>-mediated styrene homopolymerization activities are up to three orders of magnitude greater in the presence of alkenyl-, aryl-, or alkylsilanes than styrene homopolymerization in the absence of silane. All product polymers exhibit a single endothermic DSC feature between 80–105 °C, the characteristic glass transition temperature ( $T_g$ ) region for atactic polystyrene (Table 3-1, entries 1–9).<sup>17</sup>  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra exhibit characteristic broad resonances at  $\delta$  2.2 and 145 ppm, respectively, also indicating atactic polystyrene (Figure 3-1). Furthermore, monomodal GPC traces with polydispersities of  $\sim 2.0$  argue that these homopolymers are produced exclusively via a coordinative/insertive single-site pathway. Interestingly, there is insignificant incorporation of alkenylsilane into the polymer chain as a comonomer as well as insignificant polystyrene end-capping via silanolytic chain transfer<sup>18</sup>, as judged by NMR spectroscopy (Figure 3-1). Although radical polymerization processes typically result in very broad product polydispersities, under certain conditions such polymerizations can also afford narrow polydispersities.<sup>19</sup> To eliminate the possibility of radically-initiated polymerization, control polymerizations were performed with AIBN and 5-hexenylsilane and are discussed in detail below. In addition, note that

radically-initiated styrene polymerizations typically result in product polymers devoid of vinyl endgroups.<sup>11</sup> In the present polymerization systems, the polymer products contain styrenic vinyl resonances as verified by <sup>1</sup>H NMR spectroscopy. In addition, known styrene + ethylene copolymerizations were performed in the presence of organosilanes and yield copolymer products in agreement with the literature.<sup>7b,10b,c</sup> Under similar conditions, radical copolymerizations initiated with AIBN do not yield styrene + ethylene copolymers, whereas styrene + ethylene copolymerizations mediated by CGC catalysts in the presence of organosilane evidence up to 50 mol % styrene incorporation into the polyethylene chain, consistent with a coordinative/insertive pathway.<sup>7b,10b,c</sup>

**Table 3-1.** CGCTiMe<sub>2</sub>/Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>-mediated Styrene Homopolymerization

| Entry | Organosilane/<br>Comonomer | [organosilane]<br>(mM) | Activity <sup>c</sup><br>( $\times 10^4$ ) | M <sub>n</sub> <sup>d</sup> | M <sub>w</sub> /M <sub>n</sub> <sup>d</sup> | T (°C) | T <sub>g</sub> (°C) | Tacticity <sup>e</sup> |
|-------|----------------------------|------------------------|--------------------------------------------|-----------------------------|---------------------------------------------|--------|---------------------|------------------------|
| 1     | -                          | -                      | 0.10                                       | 5500                        | 1.9                                         | 25     | 104                 | atactic                |
| 2     | allylsilane                | 100                    | 18.0                                       | 5200                        | 2.0                                         | 25     | 100                 | atactic                |
| 3     | 3-butenylsilane            | 100                    | 1.00                                       | 8100                        | 2.3                                         | 23     | 85                  | atactic                |
| 4     | 5-hexenylsilane            | 200                    | 120                                        | 5600                        | 3.3                                         | 30     | 100                 | atactic                |
| 5     | 7-octenylsilane            | 100                    | 100                                        | 4400                        | 1.8                                         | 32     | 98                  | atactic                |
| 6     | <i>n</i> -hexylsilane      | 50                     | 5.20                                       | 4100                        | 1.8                                         | 28     | 100                 | atactic                |
| 7     | <i>n</i> -hexylsilane      | 100                    | 10.0                                       | 4500                        | 1.6                                         | 26     | 95                  | atactic                |
| 8     | <i>n</i> -hexylsilane      | 200                    | 11.0                                       | 3700                        | 1.7                                         | 23     | 97                  | atactic                |
| 9     | <i>n</i> -hexylsilane      | 400                    | 11.0                                       | 3700                        | 1.8                                         | 24     | 95                  | atactic                |
| 10    | di- <i>n</i> -hexylsilane  | 100                    | 10.0                                       | 3900                        | 2.0                                         | 23     | 95                  | atactic                |
| 11    | tri- <i>n</i> -hexylsilane | 100                    | 13.0                                       | 10500                       | 2.3                                         | 23     | 98                  | atactic                |
| 12    | tetramethylsilane          | 100                    | 0.10                                       | 3800                        | 2.0                                         | 24     | 102                 | atactic                |
| 13    | phenylsilane               | 100                    | 30.0                                       | 9600                        | 2.4                                         | 25     | 95                  | atactic                |
| 14    | tetraphenylsilane          | 100                    | 0                                          | -                           | -                                           | 23     | -                   | -                      |
| 15    | 1-hexene                   | -                      | 0.38                                       | 3000                        | 2.0                                         | 24     | 110                 | atactic                |

<sup>a</sup>CGC = Me<sub>2</sub>Si(Me<sub>4</sub>C<sub>5</sub>)(N<sup>t</sup>Bu); polymerization conditions: 50 mL toluene, 60 min. <sup>b</sup>cocatalyst = 10  $\mu$ mol

Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>; catalyst = 10  $\mu$ mol <sup>c</sup>Units = g/(mol Ti  $\cdot$  hr) <sup>d</sup>By GPC in 1,2,4-trichlorobenzene vs. polystyrene standards <sup>e</sup>tacticity based on <sup>13</sup>C NMR spectra.

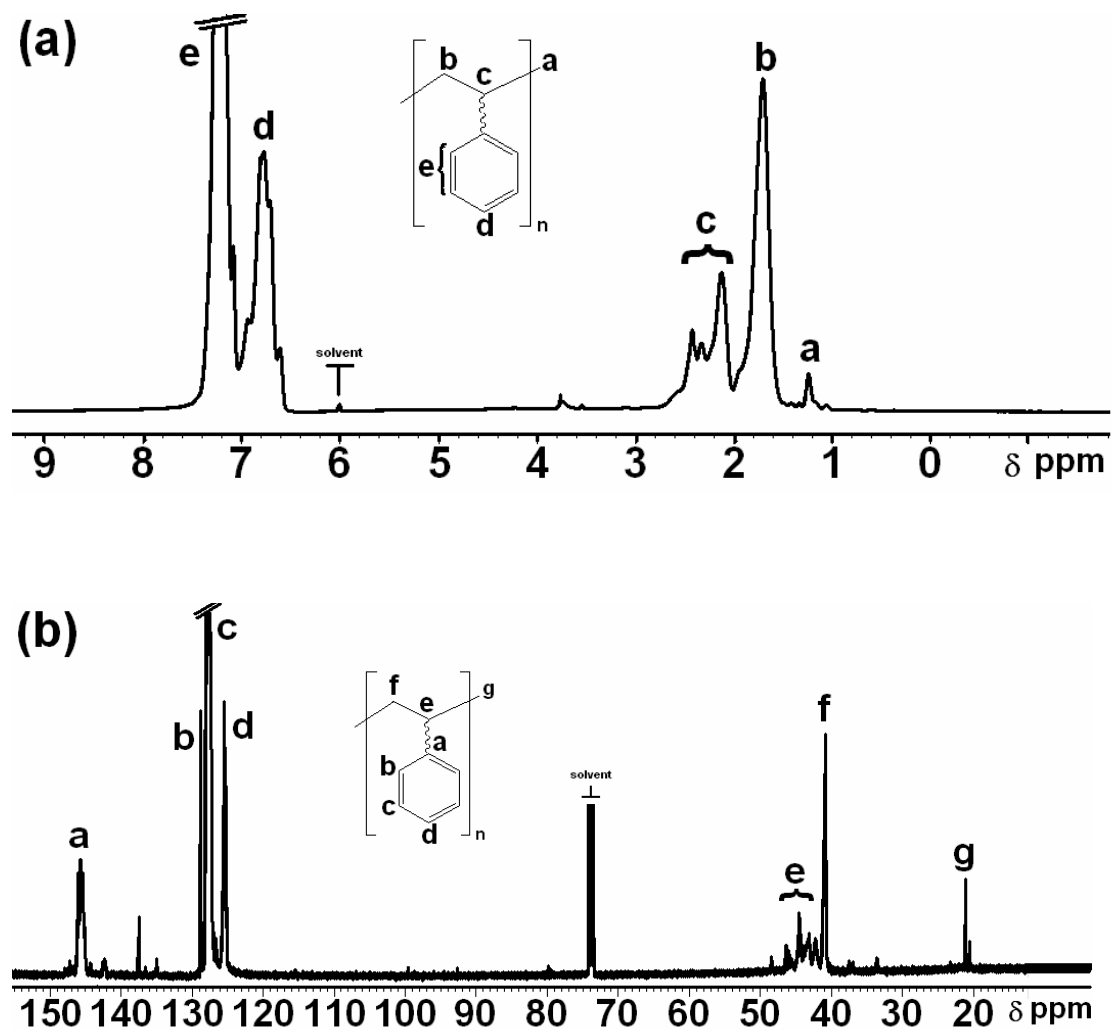
**Table 3-2.** EBICGCTi<sub>2</sub>Me<sub>4</sub>/Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>-mediated Styrene Homopolymerization

| Entry | Organosilane          | [organosilane]<br>(mM) | Activity <sup>c</sup><br>(x10 <sup>4</sup> ) | M <sub>n</sub> <sup>d</sup> | M <sub>w</sub> /M <sub>n</sub> <sup>d</sup> | T (°C) | T <sub>g</sub> (°C) | Tacticity <sup>e</sup> |
|-------|-----------------------|------------------------|----------------------------------------------|-----------------------------|---------------------------------------------|--------|---------------------|------------------------|
| 1     | -                     | -                      | 5.87                                         | 4800                        | 2.1                                         | 27     | 83                  | atactic                |
| 2     | allylsilane           | 100                    | 28.6                                         | 4100                        | 1.9                                         | 26     | 76                  | atactic                |
| 3     | 3-butenylsilane       | 100                    | 1.90                                         | 6200                        | 1.9                                         | 22     | 105                 | atactic                |
| 4     | 5-hexenylsilane       | 200                    | 1.00                                         | 3900                        | 1.7                                         | 25     | 97                  | atactic                |
| 5     | 7-octenylsilane       | 100                    | 1.00                                         | 7000                        | 1.5                                         | 25     | 98                  | atactic                |
| 6     | <i>n</i> -hexylsilane | 200                    | 2.00                                         | 4600                        | 1.9                                         | 27     | 101                 | atactic                |

<sup>a</sup>CGC = Me<sub>2</sub>Si(Me<sub>4</sub>C<sub>5</sub>)(N<sup>t</sup>Bu), EBI = Ethylene-bridged bis(indenyl); polymerization conditions: 50 mL toluene, 60 min.

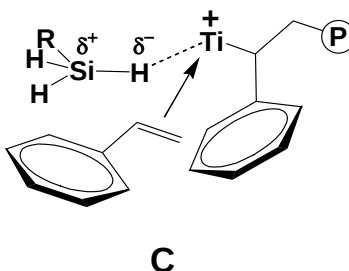
<sup>b</sup> cocatalyst = 10 μmol Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>; catalyst = 10 μmol <sup>c</sup>Units = g/(mol Ti • hr) <sup>d</sup>By GPC in 1,2,4-trichlorobenzene vs. polystyrene standards <sup>e</sup>tacticity based on <sup>13</sup>C NMR spectra.

**Figure 3-1.** (a)  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum and (b)  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum of the styrene homopolymer produced by  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  in the presence of an organosilane.



To minimize the possibility of a cationic polymerization pathway,<sup>2f,20</sup> a slight excess of catalyst over cocatalyst is always used to ensure complete  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  consumption. The homopolymers produced in the presence of the organosilane modifiers have three significant regiochemical signatures, the relative abundances of which indicate that the polystyrene is produced via a coordinative/insertive pathway (Figure 3-1b).<sup>21, 14</sup> Thus,  $^{13}\text{C}$  NMR end group analysis reveals three polystyrene microstructures. The resonance at  $\delta$  21.2 ppm indicates 2,1-insertion followed by a second 2,1-insertion of styrene monomer,<sup>16</sup> while the resonance at  $\delta$  21.8 ppm results from a 2,1-insertion followed by a 1,2-insertion of styrene monomer.<sup>16</sup> Finally, the resonance at  $\delta$  34 ppm indicates a 1,2-insertion followed by a second 1,2-insertion of monomer.<sup>7, 22</sup> The relative intensities indicate that 2,1-insertion regiochemistry predominates here.<sup>23, 24</sup>

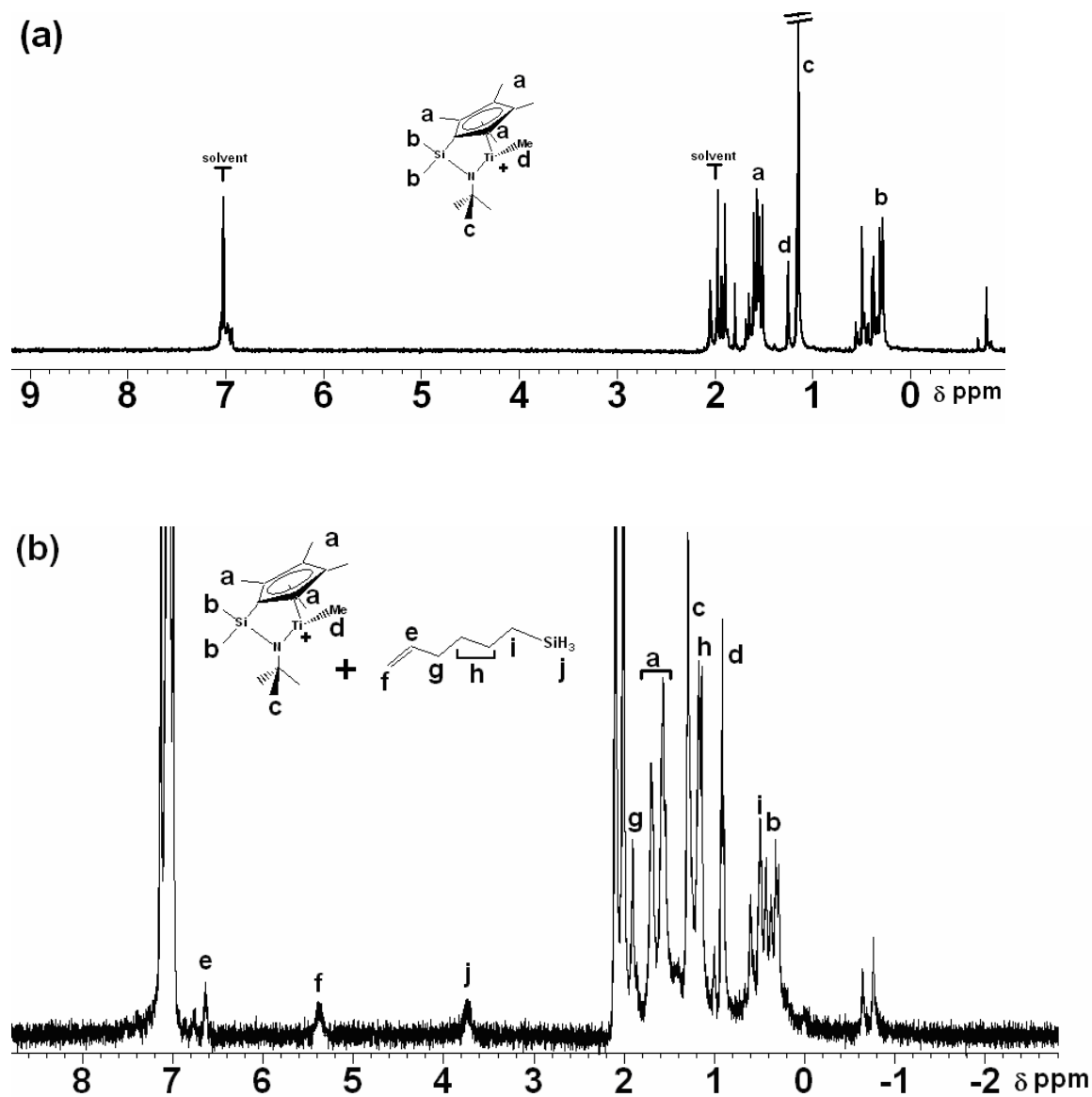
The present low activity of the control CGCTiMe<sub>2</sub>-mediated styrene homopolymerizations in the absence of organosilane is in agreement with previous results.<sup>5f, 7</sup> As noted above, the modest activity is ascribed to inactivation via intramolecular coordination of a 2,1-insertion product (e.g., **A**).<sup>6</sup> In contrast to this scenario, we suggest that weakly Lewis basic silyl groups<sup>25</sup> interfere with the “back-biting” of the last inserted styrene, thus facilitating incoming monomer coordination and enchainment, hence accelerating chain propagation (e.g., **C**).<sup>17-26</sup> This would involve interaction between the weakly Lewis basic  $-\text{SiH}_3$  group and the electrophilic Ti-center.<sup>17-18</sup>



To assess whether any changes in the fundamental catalyst structure are involved (e.g., CGCTi–N bond scission<sup>27</sup>), control experiments were performed using stoichiometric organosilane additions to CGCTiMe<sub>2</sub> and CGCTiMe<sub>2</sub>/Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>–</sup> solutions in C<sub>7</sub>D<sub>8</sub>.<sup>8</sup> Upon organosilane addition to CGCTiMe<sub>2</sub>, no reaction occurs as judged by <sup>1</sup>H NMR spectroscopy. However, upon addition of stoichiometric alkenylsilane to CGCTiMe<sub>2</sub>/Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>–</sup>, rapid Ti–C/Si–H transposition<sup>28, 29</sup> and olefin coordination are observed at –80 °C (Figure 3-2). Olefin coordination<sup>30</sup> is presumably followed by Ti–C/Si–H transposition, indicated by the gradual disappearance of the  $\delta$  3.6 (–SiH<sub>3</sub>) resonance. Furthermore, upon addition of excess alkenylsilane to CGCTiMe<sub>2</sub>/Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>–</sup> at room temperature, alkenylsilane homopolymerization occurs.<sup>8</sup> Additionally, there are no detectable changes in the *ansa*-amido ligand NMR parameters. Therefore, there is no evidence that catalyst “CGC” ligation changes upon organosilane addition, but rather the expected Ti–C/Si–H transposition and olefin coordination processes occur.

To eliminate the possibility of silyl radical-initiated styrene polymerization,<sup>11</sup> the possible reaction of 5-hexenylsilane with a solution of styrene in C<sub>7</sub>D<sub>8</sub> was investigated and no reaction was observed over a period of 3 hours by <sup>1</sup>H NMR spectroscopy. However, upon addition of CGCTiMe<sub>2</sub>/Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>–</sup> to this solution, rapid styrene polymerization occurs as observed by <sup>1</sup>H NMR spectroscopy. Furthermore, upon addition of AIBN to the unreactive styrene/5-hexenylsilane solution, rapid styrene polymerization again occurs as observed by <sup>1</sup>H NMR spectroscopy. Importantly, the atactic polystyrene produced by AIBN initiation is devoid of vinyl resonances as observed by <sup>1</sup>H NMR spectroscopy.

**Figure 3-2.** (a)  $^1\text{H}$  NMR (400 MHz,  $\text{C}_7\text{D}_8$ ) spectrum of CGCTiMe<sub>2</sub> activated with  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  at 25 °C and (b)  $^1\text{H}$  NMR (400 MHz,  $\text{C}_7\text{D}_8$ ) spectrum of CGCTiMe<sub>2</sub> activated with  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  followed by stoichiometric addition of 5-hexenylsilane at -80 °C.



To better evaluate the role of the silane hydride functionality, control polymerizations were performed with tetramethylsilane and tetraphenylsilane (Table 3-1, entries 12 and 14, respectively). Importantly, these polymerizations exhibit marginal activity and produce negligible amounts of product polymer. This result further supports the requirement for the weakly basic Si-H to disrupt the styrene “back-biting”. Tetramethylsilane was used here to ensure that the sterics associated with tetraphenylsilane are not the sole reason for the low polymerization activity and lack of “back-biting” interference. In addition, the importance of the Si-H group was investigated by performing polymerizations in the presence of di- and tri-substituted organosilanes (Table 3-1, entries 10-11). As seen from the high polymerization activities and atactic polymer microstructures, secondary and tertiary organosilanes have a very similar effect on styrene homopolymerization processes.

To further understand the role of the silyl functionality with respect to polymerization rate enhancement, a series of EBICGCTi<sub>2</sub>Me<sub>4</sub>-mediated styrene polymerization experiments was also conducted (Table 3-2). Interestingly, for EBICGCTi<sub>2</sub>Me<sub>4</sub>-mediated systems, there is *modest to negligible* change in styrene homopolymerization activity in the presence of organosilane. These results are consistent with the observation that catalyst deactivation by the last inserted styrene is not known to occur in these systems.<sup>7, 10</sup> Intriguingly, the CGCTiMe<sub>2</sub>- and EBICGCTi<sub>2</sub>Me<sub>4</sub>-derived systems do not significantly participate in organosilane chain transfer processes during styrene homopolymerization as judged from the consistency of polymer  $M_n$  even upon addition of large organosilane concentrations (up to 400 mM; Tables 3-1 and 3-2; Figure 3-1). This is consistent with the retention of fundamental CGC ligation structure in these

catalysts. Preliminary experiments also reveal that these same organosilanes have little effect on the activity of  $\text{Cp}^*\text{TiMe}_3/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  styrene polymerization catalysts.<sup>10b,d</sup>

## Conclusions

The present results show that organosilanes (including alkyl-, alkenyl-, and arylsilanes) have the capability to activate otherwise marginally active  $\text{CGCTiMe}_2$ -derived catalysts for rapid styrene homopolymerization. Organosilanes also exhibit diverse chain transfer efficiencies, depending on the catalyst architecture.

## CHAPTER 4

Organo- $f^n, d^0$ -Mediated Synthesis of Amine-Capped Polyethylenes. Scope and Mechanism

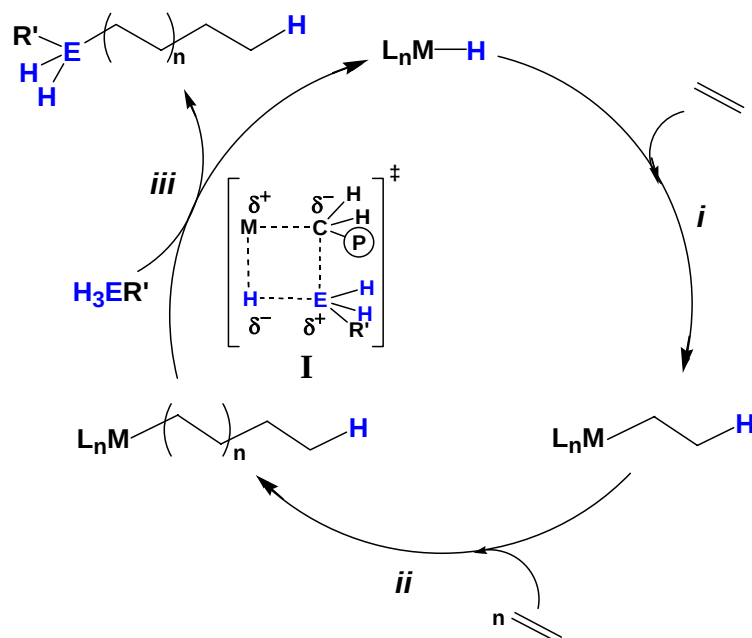
## Introduction

Polyolefins are attractive commodity materials with an impressive range of important applications.<sup>1</sup> As a consequence of their microstructural versatility, polyolefins offer a myriad of useful macromolecular properties, including, but not limited to, elasticity, melt-fracture resistance, and impressive processability. Functionalized polyolefins are also highly desirable polymeric materials due to their enhanced physical properties such as adhesion, paintability, and compatibility with diverse other materials.<sup>2</sup> There are several synthetic routes to functionalized polyolefins including post-polymerization modification,<sup>3</sup> copolymerization with polar monomers,<sup>4</sup> and catalytic chain-transfer with heteroatom reagents.<sup>5,6,7,8,9,10,11</sup> Of these approaches, post-polymerization modification presents challenges due to the unreactive nature of saturated hydrocarbon polymers as well as the lack of precise control over functionalization levels and locations. Copolymerization with polar comonomers is effective, however is generally restricted to less oxophilic, more polar reagent tolerant late transition metal catalysts, which have modest polymerization activities.

An alternative and versatile approach to polyolefin functionalization involves implementation of chain-transfer processes and agents, with the latter defined as chemical reagents which both terminate and facilitate the reinitiation of polyolefin chain growth, and can efficiently control molecular weight while simultaneously and selectively introducing heteroatom-functionality into the macromolecular architecture. To date, electron-deficient/neutral chain-transfer agents such as alanes, boranes, and silanes have been successfully introduced into catalytic single-site olefin polymerization processes. For these electron-deficient/neutral chain-transfer agents, in the simplest scenario, the heteroatom is

delivered to the polymer chain terminus at the end of a hydride-based catalytic cycle (Scheme 4-1). This catalytic cycle is envisioned to proceed via sequences of : i) insertion of C-C unsaturation into a M-H bond, ii) multiple insertions of C-C unsaturation into the resulting M-C bond(s), and iii) chain termination, presumably via a four-center  $\sigma$ -bond metathesis transition state,<sup>12</sup> to release the heteroatom-functionalized polyolefin and regenerate the active catalyst (Scheme 4-1). Scenarios have also been demonstrated which place multiple heteroatom groups in the polyolefin chain.<sup>5,6</sup>

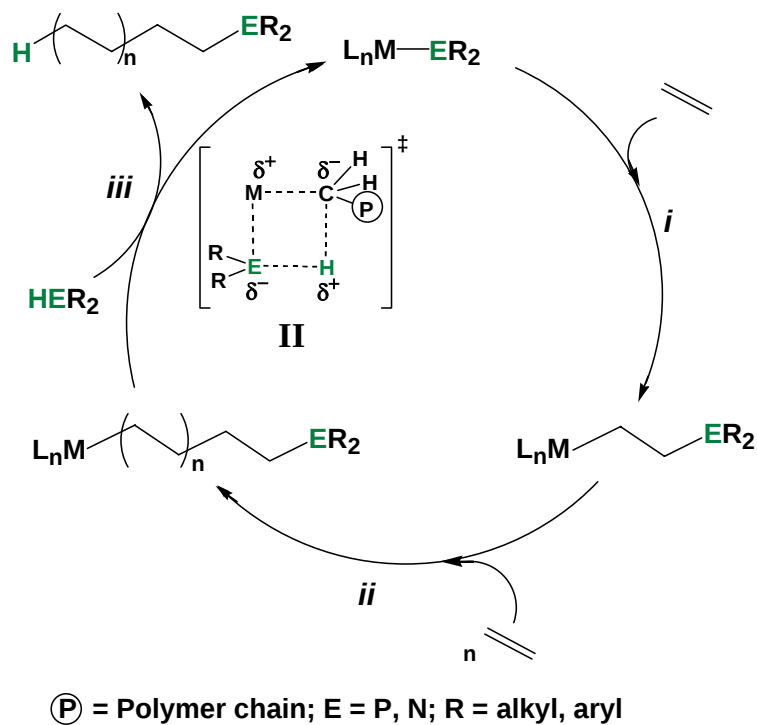
**Scheme 4-1.** Catalytic Cycle for Single-Site-Mediated Olefin Polymerization in the Presence of Monofunctional Electron-Deficient/Neutral Chain Transfer Agents.



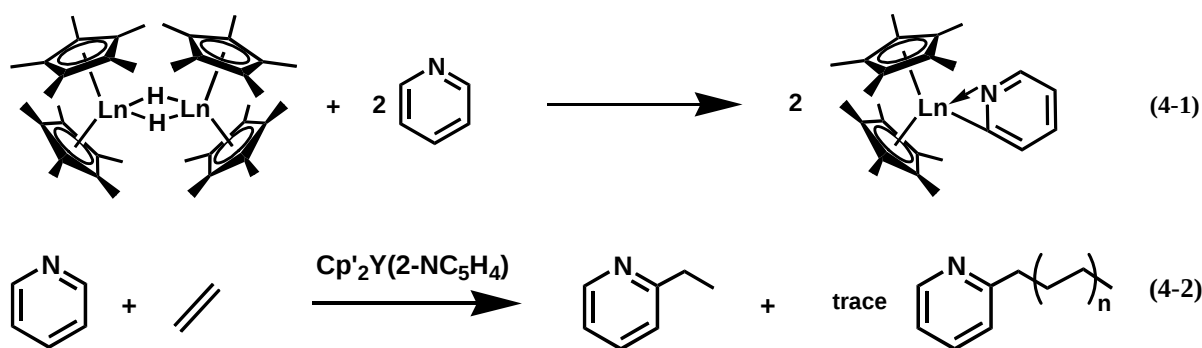
Ⓟ = Polymer chain; E = Si, B, Al; R' = alkyl, aryl

In contrast to the pathways outlined above, functionally analogous processes with electron-rich chain-transfer agents have been extensively characterized only for phosphines. Here, the catalytic cycle is envisioned to proceed via sequences of: i) insertion of C-C unsaturation into the metal-heteroatom bond, ii) multiple insertions of C-C unsaturation into the resulting M-C bond(s), and iii) protonolysis of the metal-polymeryl bond, presumably via a polar four-center  $\sigma$ -bond metathesis transition state, to release the functionalized polyolefin and regenerate the active catalyst (Scheme 4-2). While the synthesis of phosphine-terminated polyethylenes can be achieved via this route, the product polymers are generally of specialized interest. In contrast, amine-terminated polyolefins, if accessible via chain transfer routes, have broad established utility in a variety of applications including, but not limited to, drug and gene delivery, antibacterial treatments, sensors, adhesives, and ion-exchange resins.<sup>13</sup> This is the motivation for the present investigation.

**Scheme 4-2.** Catalytic Cycle for Single-Site-Mediated Olefin Polymerization in the Presence of Monofunctional Electron-Rich Chain Transfer Agents.



Organolanthanide complexes<sup>14</sup> are among the most versatile catalysts for homogeneous single-site coordinative  $\alpha$ -olefin polymerization.<sup>1</sup> Catalysts of the type  $[\text{Cp}'_2\text{LnH}]_2$ <sup>15</sup> ( $\text{Cp}' = \eta^5\text{-Me}_5\text{C}_5$ ) and  $[\text{Me}_2\text{-SiCp}''_2\text{LnH}]_2$ <sup>16</sup> ( $\text{Cp}'' = \eta^5\text{-Me}_4\text{C}_5$ ) efficiently polymerize ethylene to high molecular weight polyethylene with turnover frequencies exceeding  $1800\text{ s}^{-1}$  and with narrow product polydispersities. Previously, it was shown that  $n\text{-BuSiH}_3$ ,  $\text{C}_6\text{H}_5\text{SiH}_3$ , and  $\text{C}_6\text{H}_5\text{CH}_2\text{SiH}_3$  function as efficient chain-transfer agents for organolanthanide-catalyzed olefin homopolymerizations as well as for ethylene/ $\alpha$ -olefin copolymerizations. The established reaction pathway is represented in Scheme 4-1. In addition, although secondary organosilanes are found to be less efficient than primary organosilanes, the concentration of silane-capped polymer products increases incrementally with increasing concentration of secondary organosilane in the reaction system. Subsequently, the complex  $\text{Cp}'_2\text{Y}(\text{2-pyridyl})$  was synthesized from  $[\text{Cp}'_2\text{YH}]_2$  via a lanthanocene-mediated aryl C-H activation process (eq 4-1).<sup>17</sup> Using this complex, 2-ethylpyridine and traces of polymeric products are produced catalytically in the presence of excess ethylene and pyridine (eq 4-2).<sup>17</sup>



Recently, organolanthanide complexes have been used to selectively synthesize phosphine-capped polyethylenes with activities as high as  $10^7\text{ g polymer}/(\text{mol Ln}\cdot\text{atm}\cdot\text{h})$ . In these catalytic systems, a diverse range of secondary phosphines is found to effect selective,

catalytic C-P bond formation and chain termination, including diphenyl-, diethyl-, and di-*iso*-butylphosphine. Primary phosphines (e.g., cyclohexylphosphine) are also found to be extremely efficient chain-transfer agents, producing phosphine-capped oligoethylenes. These results demonstrate the ability of electron-rich chain-transfer agents to selectively and catalytically functionalize polyolefin chains. Based on analogies between hydrophosphination<sup>18</sup> and hydroamination,<sup>19</sup> amine chain-transfer processes would seem to be viable in single-site organolanthanide-mediated olefin polymerization catalysis. However, since Ln-C protonolyses by amines are established to be  $\sim 10^4$  x faster than by the corresponding phosphines,<sup>18b</sup> careful tuning of the amine chain-transfer agent steric and electronic characteristics is essential to achieving efficient chain propagation (Scheme 4-2, rate (i, ii)  $\gg$  rate (iii)).

In a recent preliminary report, it was communicated that organolanthanide-catalyzed ethylene polymerization in the presence of dicyclohexylamine yields dicyclohexylamine-terminated polyethylenes, demonstrating that despite kinetic disadvantages potentially incurred in amine chain transfer processes, such catalytic cycles are viable processes with judicious choice of chain transfer agents.<sup>9</sup> In the present contribution, we extend this study to include a wide range of secondary amines as chain transfer reagents having systematically varied steric and electronic characteristics, so as to more fully investigate the scope of this organolanthanide-mediated synthesis of amine-terminated polyolefins. In addition, we present a full discussion of the kinetics and mechanism of such C-N bond-forming processes, focusing on the effects of amine substitution and drawing on observations from analogous phosphine chain transfer and other hydrofunctionalization processes to place the present experimental observations in context. We also extend the scope to  $d^0$  organo-group 4 catalysts.

## Experimental

**Materials and Methods.** All manipulations of air-sensitive materials were carried out with rigorous exclusion of oxygen and moisture in flame- or oven-dried Schlenk-type glassware on a dual-manifold Schlenk line, or interfaced to a high-vacuum line ( $10^{-6}$  Torr), or in a N<sub>2</sub>-filled MBraun glovebox with a high capacity recirculator (< 1 ppm of O<sub>2</sub>; <1 ppm of H<sub>2</sub>O). Argon, hydrogen, and ethylene (Airgas, prepurified) were purified by passage through MnO oxygen-removal and Davison 4A molecular sieve columns. Hydrocarbon solvents (*n*-pentane and toluene) were dried using activated alumina columns according to the method described by Grubbs,<sup>20</sup> and were additionally vacuum-transferred from Na/K alloy immediately prior to vacuum line manipulations. Benzene-*d*<sub>6</sub>, toluene-*d*<sub>8</sub>, 1,1,2,2-tetrachloroethane-*d*<sub>2</sub>, and chloroform-*d*<sub>1</sub> were purchased from Cambridge Isotope Laboratories. Deuterated solvents used for NMR reactions were stored under argon and over Na/K alloy in vacuum-tight storage flasks and were distilled immediately prior to use. All organic starting materials were purchased from Aldrich Chemical Co. and were used without further purification unless otherwise stated. Dicyclohexylamine was dried with LiAlH<sub>4</sub> for 48 h, transferred onto Davison 4A molecular sieves 3 x, and stored in a vacuum-tight storage flask over activated Davison 4A molecular sieves. All other amine substrates (*N,N*-bis(trimethylsilyl)amine, *N*-*tert*-butyl(trimethylsilyl)amine, di-*iso*-propylamine, di-*sec*-butylamine, and aniline) were dried over CaH<sub>2</sub> for a minimum of 5 days, distilled onto Davison 4A molecular sieves 2 x, and stored in vacuum-tight storage flasks over Davison 4A molecular sieves. The monomer 1-hexene was stirred over CaH<sub>2</sub> for 5 days and distilled immediately prior to use. The organolanthanide precatalysts Cp'<sub>2</sub>LnCH(SiMe<sub>3</sub>)<sub>2</sub> (Ln = La, Sm, Y, Lu) were synthesized according to a published

procedure.<sup>15</sup> The organotitanium precatalysts  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}^t\text{Bu})\text{TiMe}_2$ <sup>21</sup> and cocatalyst  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ <sup>22</sup> were prepared by published procedures.

**Physical and Analytical Measurements.** NMR spectra were recorded on either an Inova-400 (FT, 400 MHz  $^1\text{H}$ ; 100 MHz  $^{13}\text{C}$ ) or Inova-500 (FT, 500 MHz  $^1\text{H}$ ; 125 MHz  $^{13}\text{C}$ ) instrument. Chemical shifts ( $\delta$ ) for  $^1\text{H}$  and  $^{13}\text{C}$  are referenced to internal solvent resonances and reported relative to  $\text{SiMe}_4$ . For polymer NMR characterization, 50-75 mg samples were dissolved in 0.5-0.7 mL of  $\text{C}_2\text{D}_2\text{Cl}_4$  (Cambridge Isotope Laboratories) in a 5 mL NMR tube by heating the mixture in a 120 °C oil bath. Melting temperatures of polymers were measured by DSC (DSC 2920, TA Instruments, Inc.) from the second scan with a heating rate of 20 °C/min. GPC analyses of polymer samples were performed on a Polymer Laboratories PL-GPC 220 instrument using three PLgel 10  $\mu\text{m}$  mixed columns; operation temperature, 150 °C; mobile phase, 1,2,4-trichlorobenzene (stabilized with 125 ppm BHT); flow rate, 1 mL/min). GC-MS analyses were performed on a HP 6890 instrument equipped with a Zebron ZB-5 dimethylpolysiloxane column (30 m x 250  $\mu\text{m}$  x 0.25  $\mu\text{m}$ ) interfaced to a HP 6890 mass-selective detector. MALDI-TOF MS spectra were collected on a PE Biosystems Voyager System 6050 time-of-flight mass spectrometer using a nitrogen laser for MALDI ( $\lambda = 337$  nm). The measurements were performed in the reflector mode. Dithranol was used as the matrix with a polymer concentration of ~10 mg/mL and a polymer:matrix ratio of ~1:1 by mass.

**Organolanthanide-Mediated Polymerization of Ethylene in the Presence of Dicyclohexylamine. Representative Experiment.** In the glove box, a three-necked Morton flask, which had been dried overnight at 160 °C, equipped with a large stir bar and thermocouple (Omega type K stainless steel sheathed), was charged with dry toluene (30 mL). The flask was

next attached to a high vacuum line and the toluene was freeze-thaw degassed, followed by introduction of ethylene (1.0 atm) with rapid stirring. In the glovebox,  $\text{Cp}^*_2\text{LaCH}(\text{SiMe}_3)_2$  (0.010 mmol) was placed in a dry storage tube (dried overnight at 160 °C) equipped with a stir bar and 4 mL of dry toluene. The catalyst storage tube was attached to the high vacuum line and next, dicyclohexylamine (0.20 mL) was injected into the storage tube with rapid stirring. The solution was stirred for several min after which the contents were taken up in a  $\text{N}_2$ -purged syringe. The catalyst solution was next injected through the septum-sealed polymerization flask sidearm into the rapidly stirring reaction flask. After 90 min, methanol (10 mL) was injected to quench the reaction. Excess methanol (~ 500 mL) was then used to precipitate the polymer. The product polymer (0.5 g) was collected by filtration, washed with methanol (200 mL), and dried in vacuo at 80 °C for 48 h.  $T_m = 138$  °C.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  0.98 (-CH<sub>3</sub>), 1.2-1.6 (-CH<sub>2</sub>-), 2.4 (-CH<sub>2</sub>N-), 2.7 (-CHN-).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  29.1 (-CH<sub>2</sub>-), 61 (-CH<sub>2</sub>N-).

**Organolanthanide-Mediated Polymerization of Ethylene in the Presence of Di-*iso*-propylamine. Representative Experiment.** The same procedure as for the above reaction was employed except that di-*iso*-propylamine was used as the chain transfer agent, and a 5.0 mL aliquot of the reaction mixture was reserved for analysis. Under high vacuum conditions ( $10^{-6}$  Torr), the volatile portion of the 5.0 mL aliquot was vacuum-transferred away from the nonvolatile portion (0.06 g). The volatile solution was analyzed by GC-MS, and the nonvolatile portion was analyzed by MALDI-TOF MS.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  0.88 (-CH<sub>3</sub>), 1.25 (-CH<sub>3</sub>), 1.4-1.8 (-CH<sub>2</sub>-), 2.0 (-CH<sub>2</sub>N-), 2.35 (-CH-); the products  $\text{H}(\text{CH}_2\text{CH}_2)_n\text{N}(\text{}^i\text{Pr})_2$ ,  $n = 10-17$  and  $n = 1$ , were detected by MALDI-TOF and GC-MS, respectively.

**Organolanthanide-Mediated Polymerization of Ethylene in the Presence of Di-*sec*-butylamine. Representative Experiment.** The same procedure as for the above reaction was employed, except for that di-*sec*-butylamine was used as the chain transfer agent. The products  $\text{H}(\text{CH}_2\text{CH}_2)_n \text{N}[\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)]_2$ ,  $n = 1, 2$ , were detected by GC-MS in a ~40 % yield.

**Organolanthanide-Mediated Polymerization of Ethylene in the Presence of *N,N*-bis(trimethylsilyl)amine. Representative Experiment.** The same procedure as for the above reaction was employed, except for that *N,N*-bis(trimethylsilyl)amine was used as the chain transfer agent.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  0.16 (-SiMe<sub>3</sub>), 0.94 (-CH<sub>3</sub>), 1.2-1.6 (-CH<sub>2</sub>-), 2.1 (-CH<sub>2</sub>N-), 2.4 (-CHN); the products  $\text{H}(\text{CH}_2\text{CH}_2)_n \text{N}(\text{SiMe}_3)_2$ ,  $n = 1, 2$ , were detected by GC-MS in a ~30 % yield.

**Organolanthanide-Mediated Polymerization of Ethylene in the Presence of *N-tert*-butyl(trimethylsilyl)amine. Representative Experiment.** The same procedure as for the above reaction was employed, except for that *N-tert*-butyl(trimethylsilyl)amine was used as the chain transfer agent. The products  $\text{H}(\text{CH}_2\text{CH}_2)_n \text{N}^t\text{Bu}(\text{SiMe}_3)$  (0.04 g),  $n = 6-8$  and  $n = 1$ , were detected by MALDI-TOF and GC-MS, respectively.

**Organolanthanide-Mediated Polymerization of Ethylene in the Presence of Aniline. Representative Experiment.** The same procedure as for the above reaction was employed, except that aniline was used as the chain transfer agent.

**Organolanthanide-Mediated Polymerization of Propylene in the Presence of Dicyclohexylamine. Representative Experiment.** The same procedure as for the above reaction was used except that dicyclohexylamine was used as the chain transfer agent and 1.0 atm propylene pressure was used as the monomer.

**Organolanthanide-Mediated Polymerization of 1-Hexene in the Presence of Dicyclohexylamine. Representative Experiment.** The same procedure as for the above reaction was used except that 4.0 mL of 1-hexene were injected into the flask under argon flush with rapid stirring prior to polymerization.

**NMR-scale Organolanthanide-Mediated Polymerization of Ethylene in the Presence of *n*-Propylamine. Representative Experiment.** In the glovebox, an NMR tube equipped with a Teflon valve was loaded with  $\text{Cp}'_2\text{LaCH}(\text{SiMe}_3)_2$  (4.8 mg, 8.5  $\mu\text{mol}$ ) and  $\text{C}_6\text{D}_6$  (0.6 mL). On the high-vacuum line, the tube was evacuated while frozen at  $-78^\circ\text{C}$ , and *n*-propylamine (0.06 mL, 0.73 mmol) and  $\text{C}_6\text{D}_6$  (0.2 mL) were added via syringe under an argon flush. The tube was evacuated and backfilled with Ar while frozen at  $-78^\circ\text{C}$ , and then the tube was sealed. The sample tube was warmed quickly and 1.0 atm ethylene was bubbled through the solution for 30 min. The polymerization reaction was monitored by  $^1\text{H}$  NMR spectroscopy.

**Synthesis of *N*-Eicosyldicyclohexylamine.** A 2-neck Schlenk flask was equipped with a Teflon stir bar and reflux condenser, and the set-up was attached to the Schlenk line. Under positive nitrogen pressure, 1-bromoeicosane (1.08 g, 3.0 mmol), anhydrous potassium carbonate (1.38 g, 10 mmol), and sodium iodide (0.45 g, 3.0 mmol) were placed in the flask. Next, 25 mL of ethanol were poured into the flask, and the mixture was rapidly stirred and heated to reflux for 1 h. Dicyclohexylamine (0.55 mL, 2.8 mmol) was then rapidly injected through a septum-sealed sidearm into the refluxing reaction mixture under positive nitrogen pressure. The mixture was stirred rapidly for 48 h at reflux. Next, the mixture was cooled to room temperature and filtered. The collected white solid was washed with 3 x 25 mL dichloromethane. The filtrate was evaporated under reduced pressure, and the remaining pale yellow solid was dried under vacuum.

at  $10^{-6}$  Torr for 30 min. The crude organic solid was purified by column chromatography on silica gel, eluting with a 1:1 mixture of hexane: ethyl acetate, to give a 20 % yield (~200 mg) of *N*-eicosyldicyclohexylamine.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  0.88 ( $-\text{CH}_3$ ), 1.2-1.4 ( $-\text{CH}_2-$ ), 2.4 ( $-\text{CH}_2\text{N}-$ ), 3.0 ( $-\text{CHN}-$ ).

**Organotitanium-Mediated Polymerization of Ethylene in the Presence of Dicyclohexylamine. Representative Experiment.** In the glove box, a three-necked Morton flask, which had been dried overnight at  $160^\circ\text{C}$ , equipped with a large stir bar and thermocouple, was charged with dry toluene (30 mL). The flask was next attached to a high vacuum line and the toluene was freeze-thaw degassed, followed by introduction of ethylene (1.0 atm) with rapid stirring. Next, dicyclohexylamine (0.25 mL) was rapidly injected into the flask under argon flush and with rapid stirring. In the glovebox, a 5.0 mL sample vial equipped with a septum cap was charged with 3.20 mg (0.010 mmol) of  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N}^t\text{Bu})\text{TiMe}_2$  (CGCTiMe<sub>2</sub>) and 9.22 mg (0.010 mmol)  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ . A measured amount of toluene (4.0 mL) was then syringed into the vial with a dry,  $\text{N}_2$ -purged gastight syringe. The vial was shaken for several min, the contents were taken up in the syringe, and then removed from the glovebox immediately prior to the polymerization experiment. The catalyst solution was next rapidly syringed through the septum-sealed polymerization flask sidearm into the rapidly stirring reaction flask. After 120 min, methanol (10 mL) was injected to quench the reaction. Excess methanol (~ 500 mL) was then used to precipitate the polymer. The product polymer (0.04 g) was collected by filtration, washed with methanol (200 mL), and dried in vacuo at  $80^\circ\text{C}$  for 48 h.  $T_m = 138^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  0.97 ( $-\text{CH}_3$ ), 1.2-1.5 ( $-\text{CH}_2-$ ), 1.7-1.9 (cyclohexyl  $-\text{CH}_2-$ ), 2.3 ( $-\text{CH}_2\text{N}-$ ),

3.1 (-CHN-).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  24.6 (cyclohexyl - $\text{CH}_2$ -), 29.3 (- $\text{CH}_2$ -), 54.3 (- $\text{CH}_2\text{N}$ -).

**Organotitanium-Mediated Polymerization of Propylene in the Presence of Dicyclohexylamine. Representative Experiment.** The same procedure as for the above reaction was employed, except that 1.0 atm propylene pressure was used as the monomer. The product polymer (0.20 g) was collected as described above.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  0.95 (- $\text{CH}_3$ ), 1.1-1.3 (- $\text{CH}_2$ -), 1.3 (cyclohexyl - $\text{CH}_2$ -), 1.7 (- $\text{CH}$ -), 2.4 (- $\text{CH}_2\text{N}$ -), 3.5 (-CHN-).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta$  21 (- $\text{CH}_3$ -), 29 (- $\text{CH}_2$ -), 48 (-CH-), 56 (- $\text{CH}_2\text{N}$ -).

**Organotitanium-Mediated Polymerization of Ethylene in the Presence of Di-*iso*-propylamine. Representative Experiment.** The same procedure as for the above reaction was employed, except that di-*iso*-propylamine was used as the chain-transfer agent. GC-MS of the volatile solutions revealed no detectable insertion products.

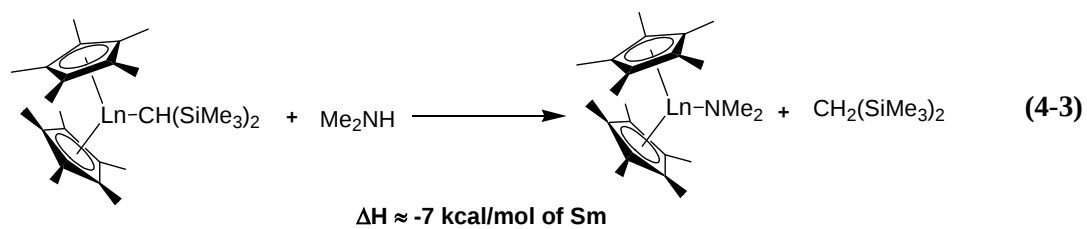
**Organotitanium-Mediated Polymerization of 1-Hexene in the Presence of Dicyclohexylamine. Representative Experiment.** The same procedure as for the above reaction was employed, except that 4.0 mL of the monomer 1-hexene was injected into the flask under an argon flush and rapid stirring, immediately prior to polymerization, and dicyclohexylamine was used as the chain-transfer agent. GC-MS of the volatile solutions revealed no detectable insertion products.

## Results

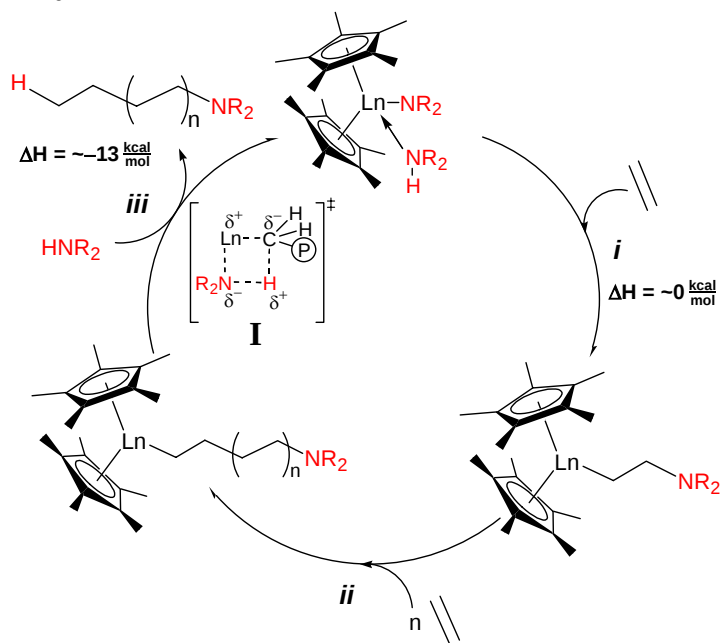
The goal of this research was to investigate the applicability scope and reaction mechanism of amines as electron-rich, C-N bond-forming chain-transfer agents in single-site olefin polymerization. Previously, we briefly communicated the catalytic synthesis of dicyclohexylamine-capped polyethylene.<sup>9</sup> In this contribution, we extend the study to include other secondary amines in both organolanthanide- and group 4-mediated polymerization systems. After a brief discussion of the catalyst activation process, in the first section we discuss the efficacy of dicyclohexyl-, di-*iso*-propyl-, di-*sec*-butyl-, *N*-*tert*-butyl(trimethylsilyl)-, and *N,N*-bis(trimethylsilyl)amine as chain transfer agents. Next, the effect of amine and lanthanide ion on polymerization characteristics will be discussed from a mechanistic standpoint. Small molecule hydroamination phenomenology will be used to understand and place in context the present observations and trends. Finally, amine chain-transfer processes in group 4-mediated olefin polymerization systems will be discussed.

**Catalyst Activation in Organolanthanide-Mediated Systems.** The chain termination step of the proposed catalytic cycle (Scheme 4-3, step *iii*) involves protonolysis of a Ln-C  $\sigma$ -bond with concomitant formation of a lanthanide-amide  $\sigma$ -bond. This step is doubtless thermodynamically favorable, as evidenced by the analogous calorimetrically characterized exothermic reaction between  $\text{Cp}'_2\text{SmCH}(\text{SiMe}_3)_2$  and  $\text{HNMe}_2$  (eq 4-3).<sup>23a</sup> The Ln-C ( $\sigma$ ) protonolysis reaction of amines with  $\text{Cp}'_2\text{LnCH}(\text{SiMe}_3)_2$  complexes is instantaneous at room temperature and has previously been found to proceed at rates up to  $10^4$  x those of the analogous phosphine reagents.<sup>18b</sup> Since formation of the  $\text{Cp}'_2\text{Ln}$ -amido precatalysts is essentially

instantaneous at room temperature, they were conveniently generated *in situ* from the corresponding hydrocarbyl complexes under typical catalytic conditions.



**Scheme 4-3.** Proposed Catalytic Cycle for Organolanthanide-Mediated Ethylene Polymerization in the Presence of Amine



**Chain-Transfer Efficiency of Dicyclohexylamine in Organolanthanide-Mediated Ethylene Polymerizations.** Dicyclohexylamine was investigated as a chain-transfer agent for organolanthanide-mediated ethylene polymerizations (Table 4-1). All polymerizations were carried out under 1.0 atm ethylene pressure using rigorously anaerobic/anhydrous conditions and procedures minimizing mass transport effects with  $\text{Cp}'_2\text{LnCH}(\text{SiMe}_3)_2$  precatalysts,<sup>15</sup> and with olefin concentrations maintained in pseudo-zero-order excess. Since polymers would be produced via ethylene insertion into the Ln-N bond, and the amine moiety is transferred to the polymer chain at the beginning of the chain growth,  $\text{Cp}'_2\text{LnNCy}_2$  ( $\text{Cp}' = \eta^5\text{-Me}_5\text{C}_5$ ;  $\text{Cy} = \text{cyclohexyl}$ ) complexes were first generated prior to polymerization. The colorless precatalyst solution remains colorless upon addition of amine chain-transfer agent and throughout the course of the polymerization reaction.

**Table 4-1.** Organolanthanide-Mediated Ethylene Polymerization in the Presence of Dicyclohexylamine

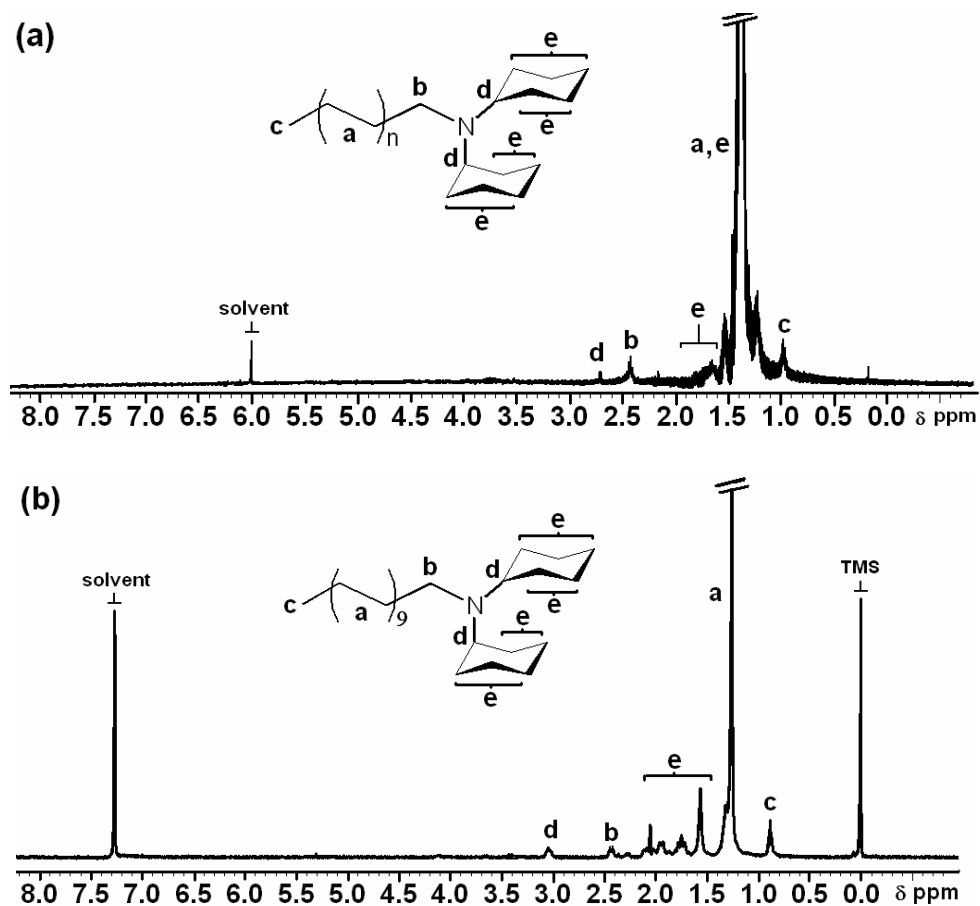
| Entry | Precatalyst <sup>a</sup>            | [Precat.]<br>( $\mu$ M) | [(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> NH]<br>(mM) | Activity <sup>b</sup><br>( $\times 10^4$ ) | M <sub>n</sub> <sup>c</sup><br>( $\times 10^3$ ) | M <sub>w</sub> /M <sub>n</sub> <sup>c</sup> | T  | T <sub>m</sub> <sup>d</sup><br>(°C) |
|-------|-------------------------------------|-------------------------|-------------------------------------------------------------|--------------------------------------------|--------------------------------------------------|---------------------------------------------|----|-------------------------------------|
| 1     | Cp' <sub>2</sub> LuR                | 370                     | 34                                                          | <0.01 <sup>e</sup>                         | -                                                | -                                           | 24 | -                                   |
| 2     | Cp' <sub>2</sub> YR                 | 330                     | 34                                                          | 0.01 <sup>e</sup>                          | -                                                | -                                           | 24 | -                                   |
| 3     | Cp' <sub>2</sub> SmR                | 330                     | 34                                                          | 0.70                                       | 260                                              | 2.7                                         | 24 | 138                                 |
| 4     | Cp' <sub>2</sub> LaR                | 360                     | 34                                                          | 1.00                                       | 200                                              | 2.5                                         | 24 | 138                                 |
| 5     | Cp' <sub>2</sub> LaNCy <sub>2</sub> | 330                     | 8.4                                                         | 2.50                                       | 1100                                             | 2.0                                         | 24 | 139                                 |
| 6     | Cp' <sub>2</sub> LaNCy <sub>2</sub> | 290                     | 20                                                          | 2.03                                       | 270                                              | 2.1                                         | 24 | 138                                 |
| 7     | Cp' <sub>2</sub> LaNCy <sub>2</sub> | 350                     | 42                                                          | 0.91                                       | 130                                              | 1.7                                         | 25 | 139                                 |
| 8     | Cp' <sub>2</sub> LaNCy <sub>2</sub> | 360                     | 84                                                          | 0.20                                       | 91                                               | 1.6                                         | 25 | 137                                 |
| 9     | Cp' <sub>2</sub> LaNCy <sub>2</sub> | 360                     | 126                                                         | 0.10                                       | 53                                               | 2.1                                         | 24 | 138                                 |

<sup>a</sup>Cp' = Me<sub>5</sub>C<sub>5</sub> ; polymerization conditions: 30 mL toluene, 90 min. <sup>b</sup>Units = g/(mol Ln • atm ethylene • h)

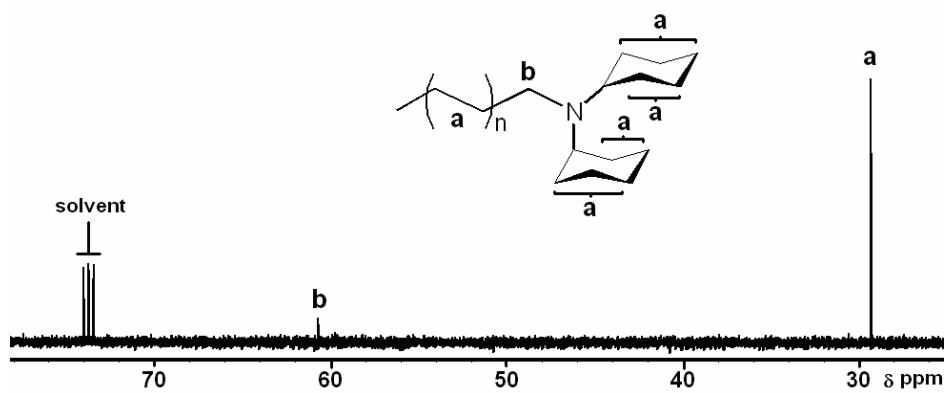
<sup>c</sup> By GPC in 1,2,4-trichlorobenzene vs. polyethylene standards <sup>d</sup>By DSC <sup>e</sup>Trace yields of polymer obtained (<10 mg). Cy = cyclohexyl; R= CH(TMS)<sub>2</sub> or secondary amine.

$^1\text{H}$  NMR spectra of the product amine-terminated polyethylenes produced using *in situ* generated  $\text{Cp}'_2\text{LaNCy}_2$  (Cy = cyclohexyl) exhibit characteristic  $-\text{CH}_2\text{N}$ ,  $-\text{CHN}$  amine ( $\delta$  2.41, 2.7, respectively),  $-\text{CH}_2-$  polyethylene backbone ( $\delta$  1.2-1.5), and  $-\text{CH}_3$  chain end ( $\delta$  0.98) resonances (Figure 4-1a), while  $^{13}\text{C}$  NMR spectra likewise exhibit characteristic amine ( $\delta$  61) and polyethylene backbone ( $\delta$  29) resonances (Figure 4-2). Furthermore, the absence of vinylic resonances in both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra argues that chain termination via  $\beta$ -hydride elimination is insignificant, while the  $\sim 1 : 1$   $-\text{CH}_2\text{N} : -\text{CH}_3$   $^1\text{H}$  NMR chain end resonance ratio argues that one amine functional group is delivered to the terminus of each polyethylene chain. The  $^1\text{H}$  NMR spectrum of the model compound *N*-eicosyldicyclohexylamine (Figure 4-1b) is in good agreement with the polymer spectral structural assignments. In addition, the resulting amine-capped polyethylenes have narrow, monomodal polydispersities, consistent with a single-site process (Table 4-1; see more below).

**Figure 4-1.**  $^1\text{H}$  NMR spectra of: (a) a dicyclohexylamine-capped polyethylene ( $M_n = 131,600$ ) produced by  $\text{Cp}^*_2\text{La}$ -mediated polymerization (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) and (b) *N*-eicosyldicyclohexylamine model compound (400 MHz,  $\text{CDCl}_3$ ).

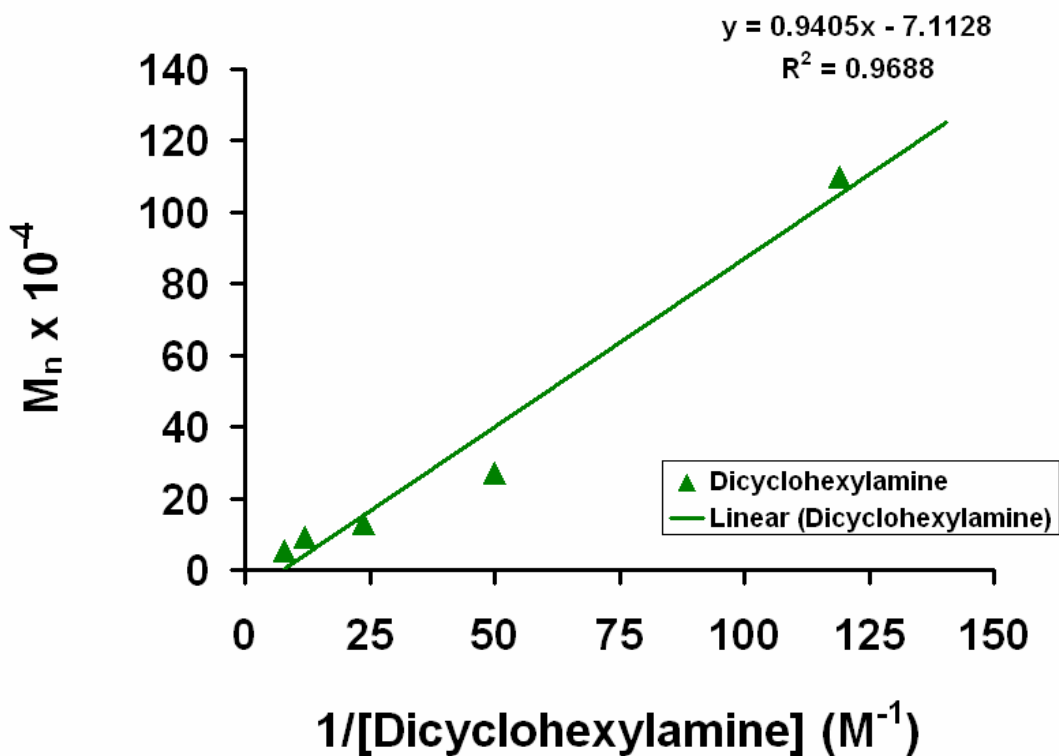


**Figure 4-2.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum of a dicyclohexylamine-capped polyethylene ( $M_n = 131,600$ ) produced by  $\text{Cp}'_2\text{La}$ -mediated ethylene polymerization.



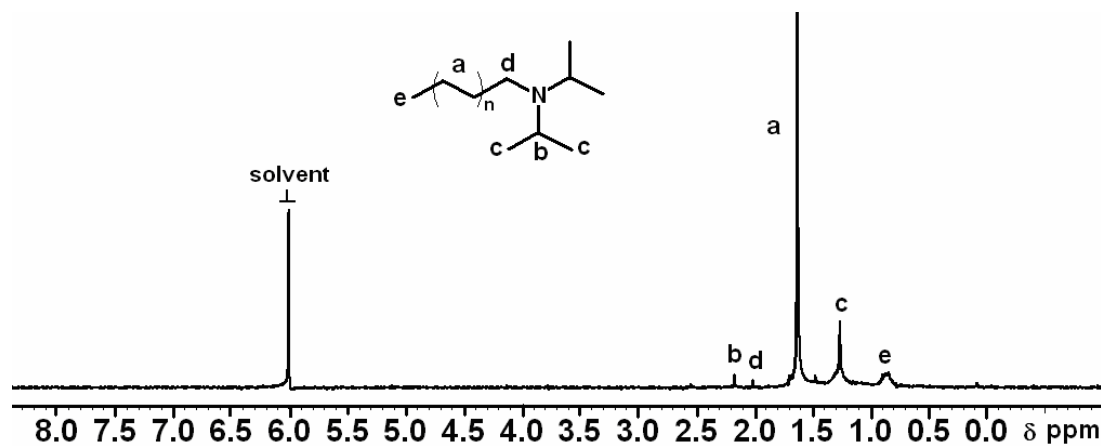
For polymerizations conducted in the presence of dicyclohexylamine, lanthanide ionic radius and polymer molecular weight appear to be inversely related. Ethylene polymerizations mediated by *in situ* generated  $\text{Cp}'_2\text{LaNCy}_2$  in the presence of dicyclohexylamine (~34 mM) require relatively long reaction times to produce significant amounts of polymer with slightly lower molecular weight ( $M_n = 200,000$ ; Table 4-1, entry 4) versus the polyethylenes produced by  $\text{Cp}'_2\text{SmNCy}_2$  ( $M_n = 260,000$ ; Table 4-1, entry 4). Furthermore, at constant  $\text{Cp}'_2\text{LaNCy}_2$  and ethylene concentrations, product polyethylene molecular weight is inversely proportional to amine concentration (Table 4-1, entries 5-9, Figure 4-3), supporting the chain-transfer mechanism shown in Scheme 4-3. Dicyclohexylamine was also investigated as a chain-transfer agent in propylene and 1-hexene homopolymerization systems using  $\text{Cp}'_2\text{LnCH}(\text{SiMe}_3)_2$  ( $\text{Ln} = \text{La}$ ) as the precatalyst. MALDI-TOF and GC-MS analyses of both quenched polymerization mixtures indicate no significant quantities of  $\alpha$ -olefin insertion products. Additional mechanistic insights are presented in the Discussion Section.

**Figure 4-3.** Relationship of polyethylene number average molecular weight (GPC versus polyethylene) to inverse  $(C_6H_{11})_2NH$  concentration at fixed catalyst and ethylene concentrations.

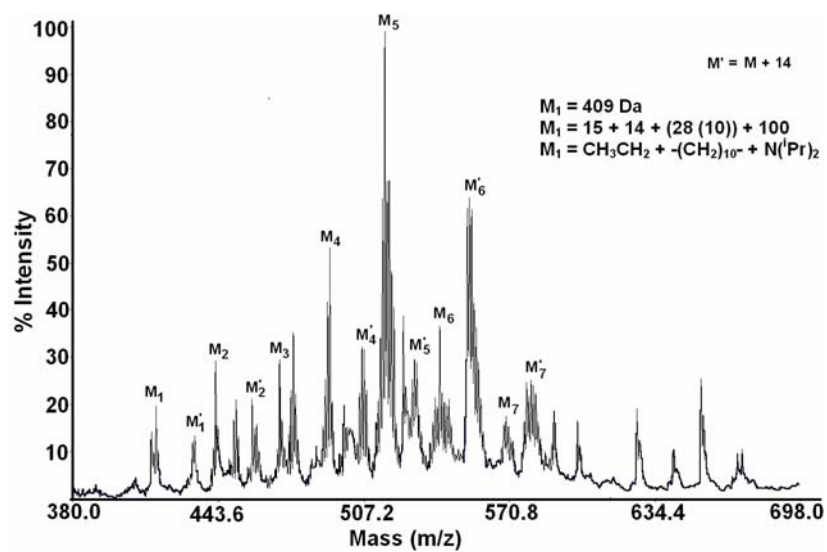


**Chain-Transfer Efficiency of Di-*iso*-propylamine in Organolanthanide-Mediated Ethylene Polymerizations.** Di-*iso*-propylamine was also investigated as a chain-transfer agent for ethylene polymerization using  $\text{Cp}'_2\text{LnCH}(\text{SiMe}_3)_2$  ( $\text{Ln} = \text{La}$ ) as the precatalyst. In situ generated  $\text{Cp}'_2\text{LaN}^i\text{Pr}_2$  is colorless, similar to the corresponding  $\text{Cp}'_2\text{LnCH}(\text{SiMe}_3)_2$  alkyls, and during the course of the polymerization the reaction solution remains colorless. The  $^1\text{H}$  NMR spectrum of the di-*iso*-propylamine-terminated oligoethylenes exhibit characteristic  $-\text{CH}_2\text{N}$ -amine ( $\delta$  2.5),  $-\text{CH}_2-$  polyethylene backbone ( $\delta$  1.2-1.4), and  $-\text{CH}_3$  chain-end ( $\delta$  0.91) resonances (Figure 4-4). The concentration of vinyl chain-end resonances in the  $^1\text{H}$  NMR spectrum is below the detection limits, again indicating that chain termination via  $\beta$ -hydride elimination is negligible and that di-*iso*-propylamine chain transfer is the dominant chain transfer pathway. Furthermore, MALDI- TOF analysis of the product oligoethylenes indicates 10-17 ethylene insertions per di-*iso*-propylamine chain-end (Figure 4-5). GC-MS analysis of the volatile portion reveals trace mono-ethylene insertion product.

**Figure 4-4.**  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum of a di-*iso*-propylamine-capped oligoethylene produced by  $\text{Cp}'_2\text{La}$ -mediated ethylene polymerization.

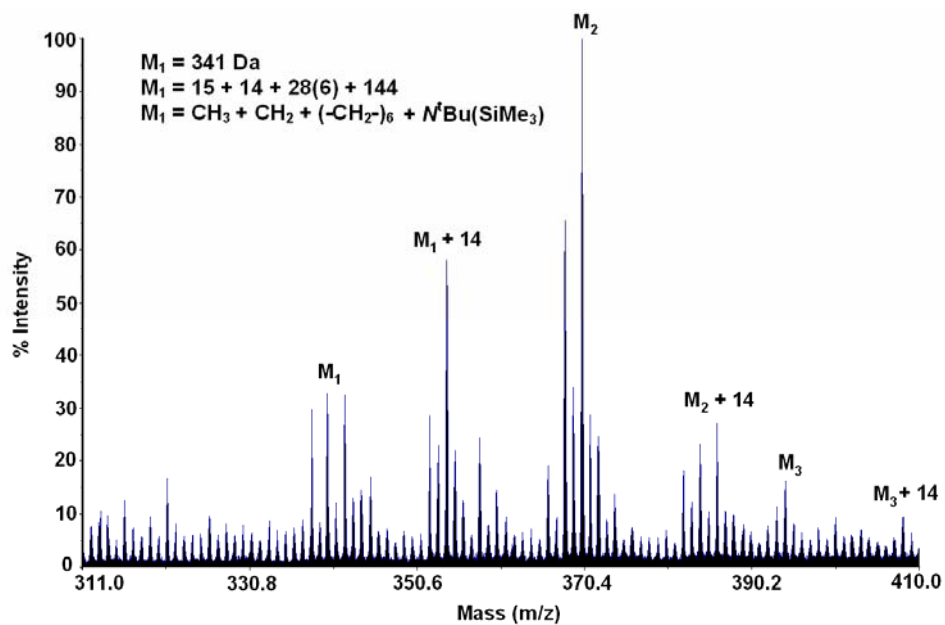


**Figure 4-5.** MALDI-TOF mass spectrum of a di-*iso*-propylamine-capped oligoethylene produced by  $\text{Cp}^*\text{La}$ -mediated ethylene polymerization.

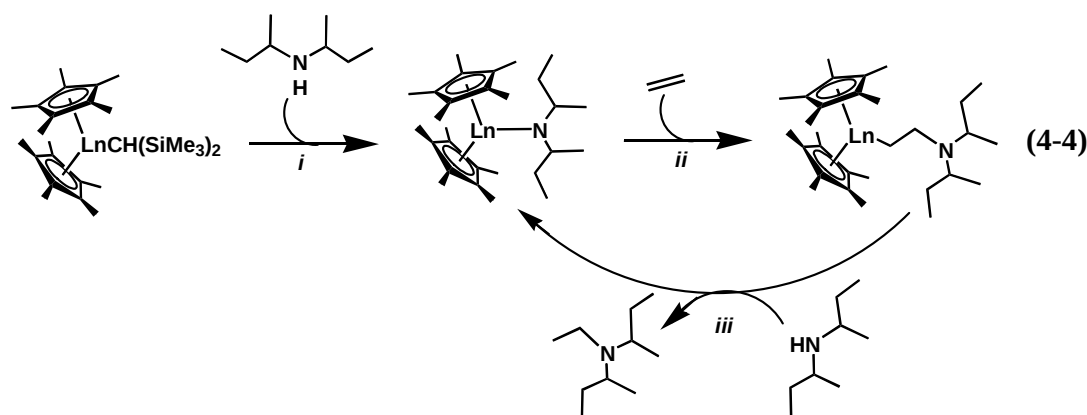


**Chain-Transfer Efficiency of *N*-tert-butyl(trimethylsilyl)amine in Organolanthanide-Mediated Ethylene Polymerizations.** *N*-tert-butyl(trimethylsilyl)amine was also investigated as a chain-transfer agent using  $\text{Cp}'_2\text{LnCH}(\text{SiMe}_3)_2$  ( $\text{Ln} = \text{La}$ ) as the precatalyst. In situ generated  $\text{Cp}'_2\text{LaN}(\text{tBu})(\text{SiMe}_3)$  is colorless, similar to the corresponding alkyls ( $\text{Cp}'_2\text{LnCH}(\text{SiMe}_3)_2$ ), and during the course of the polymerization the reaction solution remains colorless. The MALDI-TOF analyses of the product oligomeric material indicate 6-8 ethylene insertions per *N*-tert-butyl(trimethylsilyl)amine chain-end (Figure 4-6). The GC-MS analysis of the volatile portion reveals trace mono-ethylene insertion product.

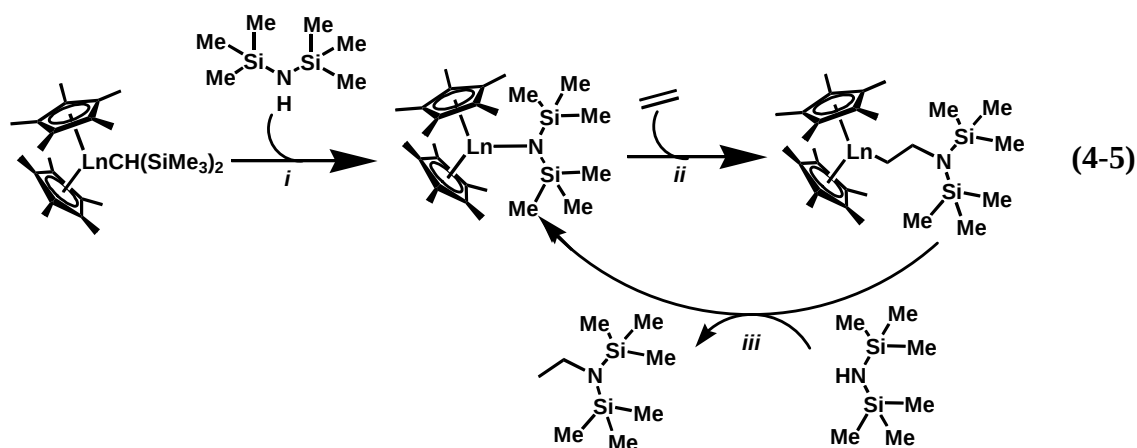
**Figure 4-6.** MALDI-TOF mass spectrum of an *N*-*tert*-butyl(trimethylsilyl)amine-capped oligoethylene produced by  $\text{Cp}^*\text{La}$ -mediated ethylene polymerization.



**Chain-Transfer Efficiency of Di-*sec*-butylamine in Organolanthanide-Mediated Ethylene Polymerizations.** Di-*sec*-butylamine was also investigated as a chain-transfer agent using  $\text{Cp}'_2\text{LnCH}(\text{SiMe}_3)_2$  ( $\text{Ln} = \text{La}$ ) as the precatalyst. In situ generated  $\text{Cp}'_2\text{LaN}^{\text{sec}}\text{Bu}_2$  is colorless, similar to the corresponding alkyls ( $\text{Cp}'_2\text{LnCH}(\text{SiMe}_3)_2$ ), and during the course of the polymerization the reaction solution remains colorless. The MALDI-TOF analyses of the quenched polymerization mixtures indicate no oligomeric ethylene insertion products; however, GC-MS analysis of this same reaction mixture indicates a mono-ethylene insertion product in  $\sim 40\%$  yield (eq 4-4).



**Chain-Transfer Efficiency of *N,N*-Bis(trimethylsilyl)amine in Organolanthanide-Mediated Ethylene Polymerizations.** *N,N*-Bis(trimethylsilyl)amine was also investigated as a chain-transfer agent using  $\text{Cp}'_2\text{LnCH}(\text{SiMe}_3)_2$  ( $\text{Ln} = \text{La}$ ) as the precatalyst. In situ generated  $\text{Cp}'_2\text{LaN}(\text{SiMe}_3)_2$  is colorless, similar to the corresponding alkyls ( $\text{Cp}'_2\text{LnCH}(\text{SiMe}_3)_2$ ), and during the course of the polymerization the reaction solution remains colorless. The MALDI-TOF analyses of the quenched polymerization mixtures indicate no oligomeric ethylene insertion products; however, GC-MS analysis of this same reaction mixture indicates a mono-ethylene insertion product in  $\sim 30\%$  yield (eq 4-5).

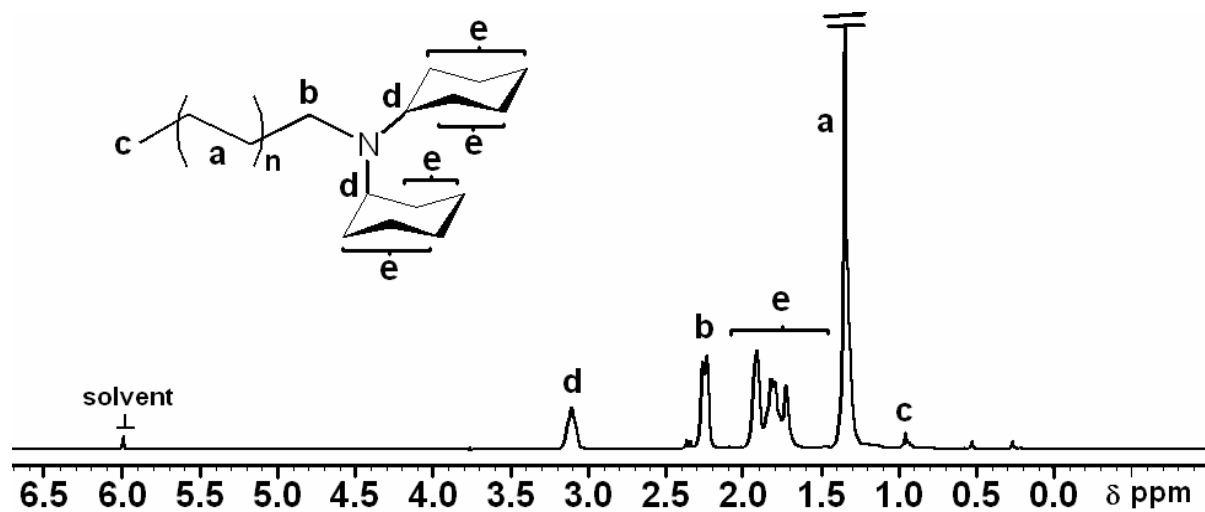


**Chain-Transfer Efficiency of Primary Amines in Organolanthanide-Mediated Ethylene Polymerizations.** Aniline and *n*-propylamine were also investigated as a chain-transfer agents using  $\text{Cp}'_2\text{LnCH}(\text{SiMe}_3)_2$  ( $\text{Ln} = \text{La}$ ) as the precatalyst. In situ generated  $\text{Cp}'_2\text{LaNHR}$  complexes are colorless, similar to the corresponding alkyls ( $\text{Cp}'_2\text{LnCH}(\text{SiMe}_3)_2$ ), and during the course of the polymerization the reaction solutions remain colorless. The MALDI-TOF, GC-MS, and  $^1\text{H}$  NMR analyses of the quenched polymerization mixtures indicate no detectable ethylene insertion products.

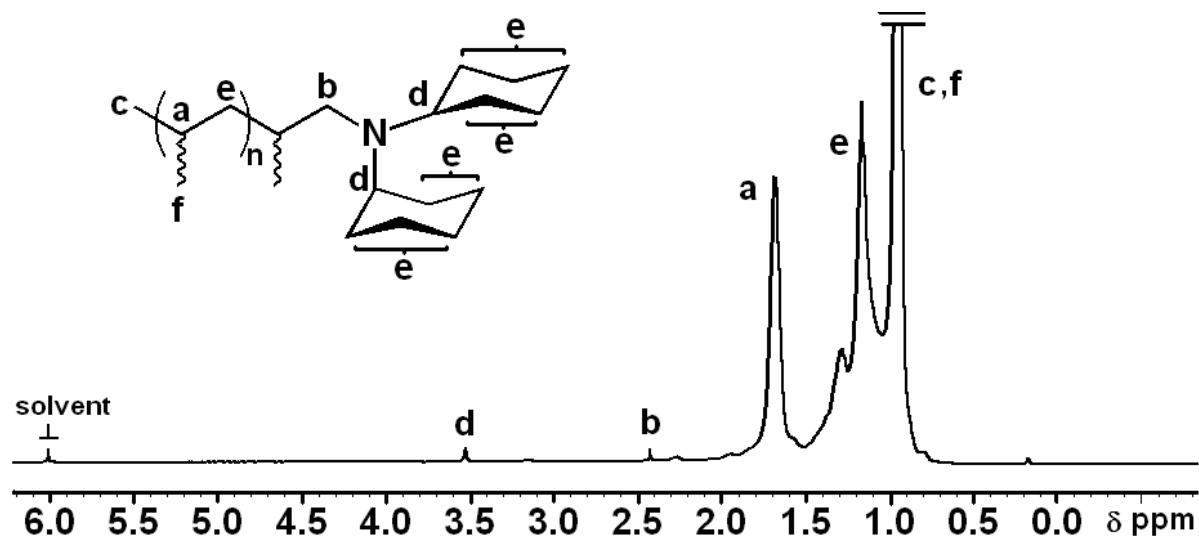
**Chain-Transfer Efficiency of Secondary Amines in Organotitanium-Mediated Olefin Polymerizations.** Dicyclohexylamine and di-*iso*-propylamine were investigated as chain-transfer agents for  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -mediated ethylene and propylene homopolymerizations. All polymerizations were performed under 1.0 atm monomer pressure and rigorously anaerobic/anhydrous conditions using procedures minimizing mass-transport effects, and with olefin concentration held constant and the chain-transfer agent maintained in pseudo-zero-order excess. The orange active catalyst solutions remain brightly colored throughout the course of the polymerization reactions, indicating the presence of a stable active species.  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -mediated olefin polymerizations in the presence of dicyclohexylamine produce small amounts ( $\sim 30\text{--}40$  mg) of product polymers with activities up to  $10^4$  g polymer/(mol of Ti  $\cdot$  atm monomer  $\cdot$  h).  $^1\text{H}$  NMR spectra of the product dicyclohexylamine-terminated polyethylenes produced by  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  exhibit characteristic  $-\text{CH}_2\text{N}$ ,  $-\text{CHN}$  amine ( $\delta$  2.3, 3.1, respectively),  $-\text{CH}_2-$  polyethylene backbone ( $\delta$  1.2–1.5), and  $-\text{CH}_3$  chain end ( $\delta$  0.97) resonances (Figure 4-7). The absence of vinylic resonances in the  $^1\text{H}$  NMR spectra argues that chain termination via  $\beta$ -hydride elimination is

insignificant. Additionally,  $^1\text{H}$  NMR spectra of the product dicyclohexylamine-terminated polypropylenes produced by  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$  exhibit characteristic  $-\text{CH}_2\text{N}$ ,  $-\text{CHN}$  amine ( $\delta$  2.4, 3.5, respectively),  $-\text{CH}_2-$  backbone ( $\delta$  1.1-1.3),  $-\text{CH}$  backbone ( $\delta$  1.7), and  $-\text{CH}_3$  backbone and chain end ( $\delta$  0.95) resonances (Figure 4-8). The absence of olefinic resonances in the  $^1\text{H}$  NMR spectra again argues that chain termination via  $\beta$ -hydride elimination is insignificant. Interestingly,  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -mediated olefin polymerizations in the presence of di-*iso*-propylamine produce no detectable insertion products by GC-MS.  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -mediated 1-hexene polymerizations in the presence of dicyclohexylamine also produce no detectable insertion products by GC-MS.

**Figure 4-7.**  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum of a dicyclohexylamine-capped polyethylene produced by  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -mediated ethylene polymerization.



**Figure 4-8.**  $^1\text{H}$  NMR (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) spectrum of a dicyclohexylamine-capped atactic polypropylene produced by  $\text{CGCTiMe}_2/\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -mediated propylene polymerization.



### Summary of Scope of Amine Chain Transfer in Organo- $f^n, d^0$ -Mediated Olefin

**Polymerization.**  $Cp'_2LnNR_2$  ( $Ln = La, Sm$ ) complexes mediate the polymerization of ethylene with good activity in the presence of secondary amines. However, the successful synthesis of amine-terminated polyethylenes is highly dependent upon both the amine and lanthanide ion employed. For example, regardless of lanthanide ion, coupled polymerization and amine-chain transfer does not appear to be efficient in the presence of the primary amines aniline and *n*-propylamine. Thus,  $Cp'_2LnNHR$ -mediated ( $Ln = La, Sm$ ) polymerizations conducted in the presence of aniline or *n*-propylamine produce no detectable ethylene insertion products. However, di-*sec*-butylamine and *N,N*-bis(trimethylsilyl)amine are both found to be efficient chain transfer agents for  $Cp'_2LaNR_2$ -mediated ethylene polymerizations, producing mono-ethylene insertion products in 40 % and 30 % yield, respectively. Interestingly, under identical reaction conditions with  $Cp'_2LaNR_2$ , di-*iso*-propylamine and *N-tert*-butyl(trimethylsilyl)amine afford amine-terminated oligoethylenes having 6-17 ethylene insertions. In contrast to the aforementioned systems, dicyclohexylamine offers the correct balance of steric bulk and electron-donating alkyl groups to produce amine-terminated high molecular weight polyethylenes in  $Cp'_2LnNR_2$  ( $Ln = La, Sm$ ) -catalyzed systems. Interestingly, the smaller lanthanide ions,  $Y^{+3}$  and  $Lu^{+3}$ , are extremely sluggish in this process and afford only trace amounts of polymer.  $Cp'_2LaNR_2$ -mediated 1-hexene and propylene homopolymerizations in the presence of secondary amines do not afford detectable quantities of insertion products under reaction conditions that afford good yields of amine-functionalized polyethylenes.

In regard to group 4 catalysts, it is found that  $CGCTiMe_2/Ph_3C^+B(C_6F_5)_4^-$ -mediated ethylene and propylene homopolymerizations in the presence of dicyclohexylamine produce

small amounts of amine-functionalized product polymers, whereas similar systems in the presence of di-*iso*-propylamine afford no detectable insertion products. Finally, CGCTiMe<sub>2</sub>/Ph<sub>3</sub>C<sup>+</sup>B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>-mediated 1-hexene polymerizations in the presence of dicyclohexylamine again produce no detectable insertion products.

## Discussion

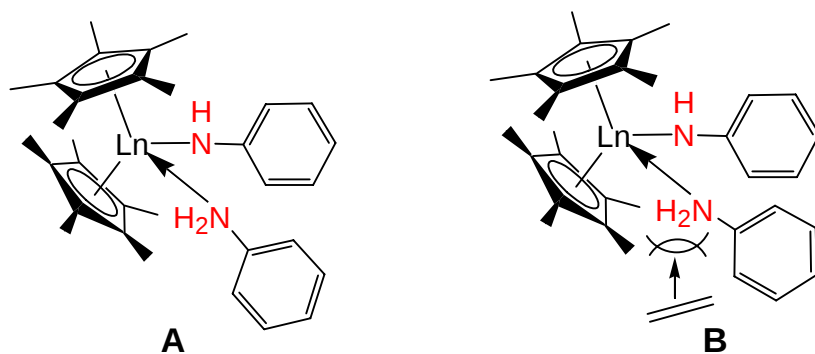
As a prelude to a detailed discussion of polymerization kinetics and mechanism in the presence of amines, it is useful to outline key constraints on the present catalytic processes. First, note that the olefin insertion barrier must be adequately low to allow ethylene insertion into the Ln-amido bond at acceptable rates (step *i*, Scheme 4-3). Second, if initial insertion is viable, then subsequent insertions must be faster than chain-terminating protonolysis for efficient polymer chain growth (step *ii*, Scheme 4-3). Third, if ethylene insertion is rapid, then chain-terminating protonolysis rates must be sufficient to control the product polymer chain length (step *iii*, Scheme 4-3). We summarize the interplay of these processes here and discuss their dependence on amine steric and electronic properties. Additionally, we compare and contrast analogous processes involving phosphines to better understand the present trends and observations.

**Amine Steric and Electronic Effects on Ethylene Polymerization.** The present results indicate that the efficacy of protonolytic chain termination in amine chain-transfer processes during lanthanocene-mediated ethylene polymerizations decreases in the order:

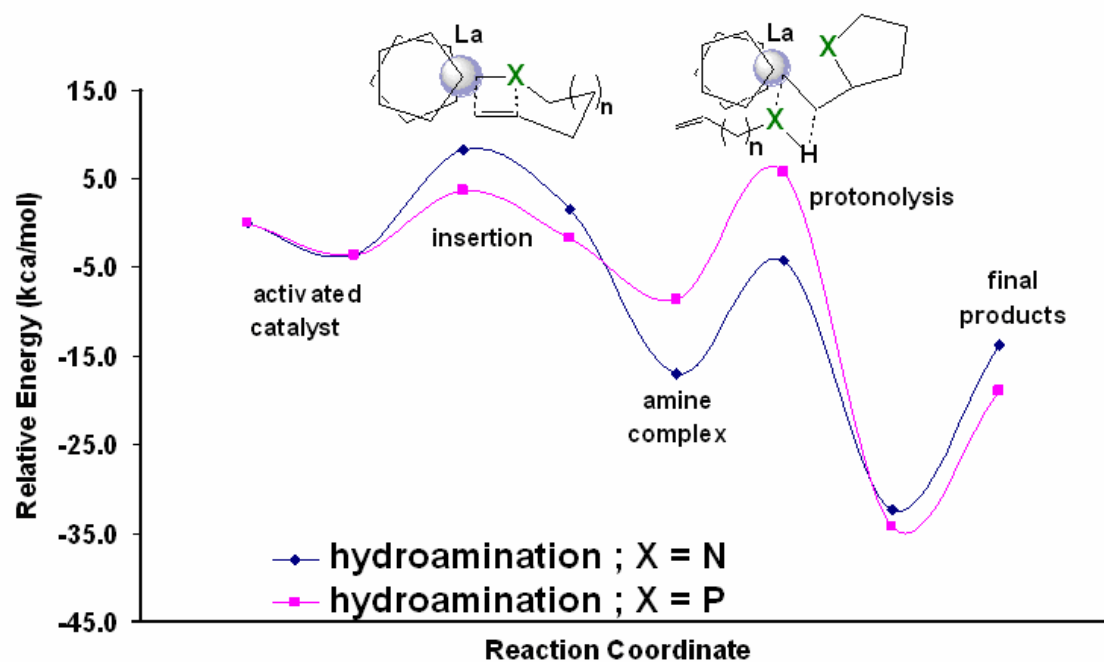


This trend doubtless reflects a complex interplay of steric and electronic characteristics that contribute to chain-transfer efficiency in these systems.

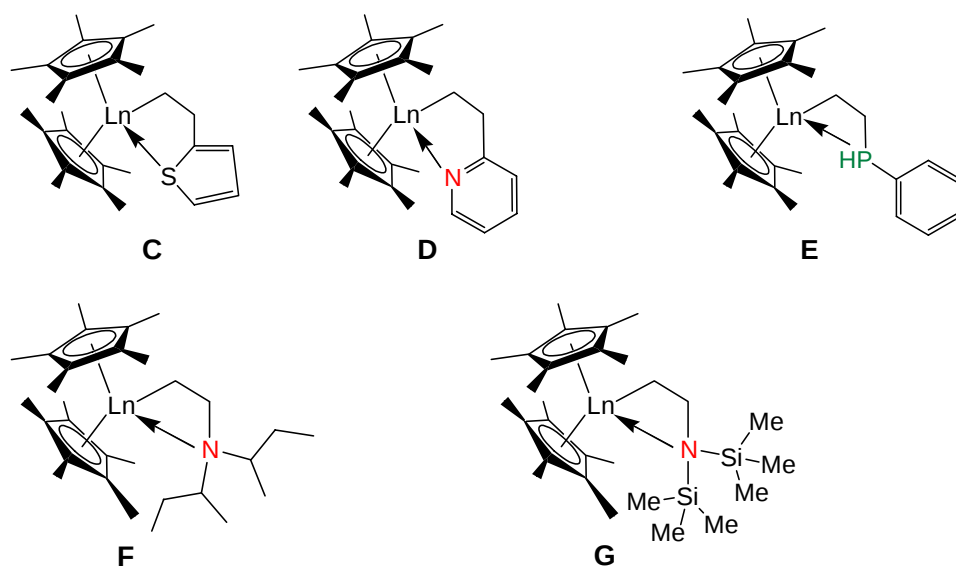
*Step i.* Unlike lanthanocene-mediated polymerizations conducted in the presence of secondary alkyl- and alkylsilylamines, the primary amines aniline and *n*-propylamine produce no detectable ethylene insertion products (Scheme 4-3, step *i*). Since these amines are the sterically least encumbered of those investigated, it is reasonable that a coordinatively saturated Ln-amido-amine complex<sup>19</sup> is kinetically inert with respect to ethylene insertion (Scheme 4-3, step *i* rate  $\ll$  step *iii* rate; representative structures **A** and **B** for the aniline case). Additionally, DFT/B3LYP-level theoretical calculations on hydrofunctionalization processes indicate that Ln-NR<sub>2</sub> complexes have higher olefin insertion barriers ( $\sim 5$  kcal/mol, Figure 4-9) than do Ln-PR<sub>2</sub> complexes,<sup>24,25</sup> while calorimetrically determined thermochemical data indicate that the Sm-N bond enthalpy in Cp'<sub>2</sub>Sm-NMe<sub>2</sub> ( $\sim 48$  kcal/mol) is far greater than the Sm-P bond enthalpy in Cp'<sub>2</sub>Sm-PEt<sub>2</sub> ( $\sim 32$  kcal/mol).<sup>23a</sup>



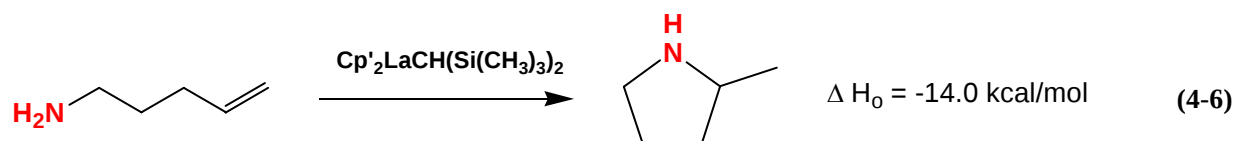
**Figure 4-9.** Modified hydrophosphination SCF energy profile compared with that for analogous hydroamination/cyclization. Adapted from reference 25.

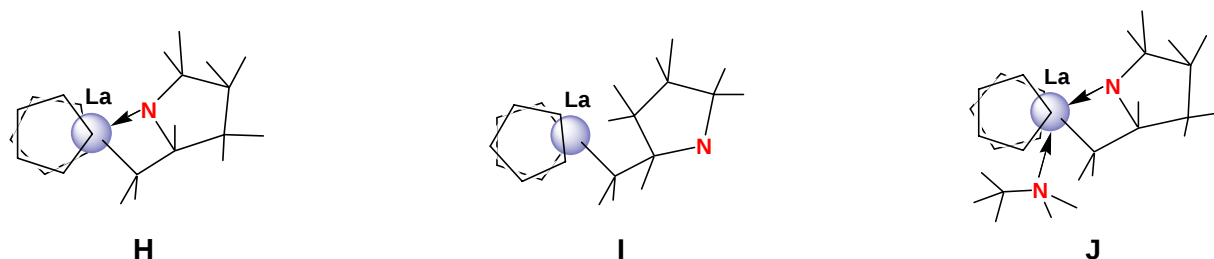


*Step ii.* Regarding the frequent observation of monoinsertion products here, note that in the cases of thiophene,<sup>10</sup> pyridine,<sup>17</sup> and phenylphosphine chain-transfer agents,<sup>8</sup> monoinsertion products are found to be particularly stable toward further ethylene insertion, likely a consequence of intramolecular heteroatom coordination to the electrophilic Ln center (e.g., **C-E**). Therefore, it is possible in the present case that the monoinsertion products  $\text{Cp}'_2\text{LaCH}_2\text{CH}_2\text{N}^{\text{sec}}\text{Bu}_2$  and  $\text{Cp}'_2\text{LaCH}_2\text{CH}_2\text{N}(\text{Si}(\text{CH}_3)_3)_2$  are also less reactive toward ethylene insertion due to stabilizing intramolecular amine coordination (e.g., **F** and **G**, respectively; step *ii* rate  $\ll$  step *i* rate, Scheme 4-3). In this connection, the DFT/B3LYP level theoretical studies on



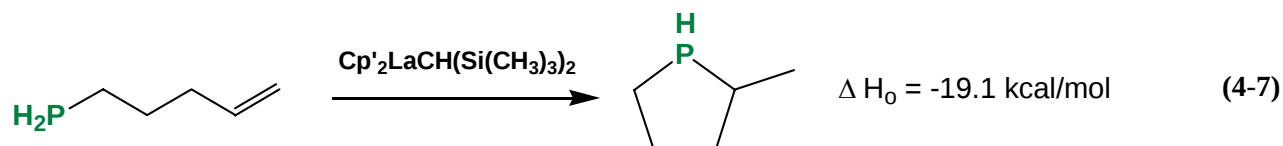
the geometries and stabilities of the intermediates and transition states in organolanthanide-catalyzed hydroamination/cyclization of 1-aminopent-4-ene (eq 4-6) find two stable product conformations, **H** and **I**, following initial intramolecular olefin insertion into the La-N bond.<sup>24</sup>



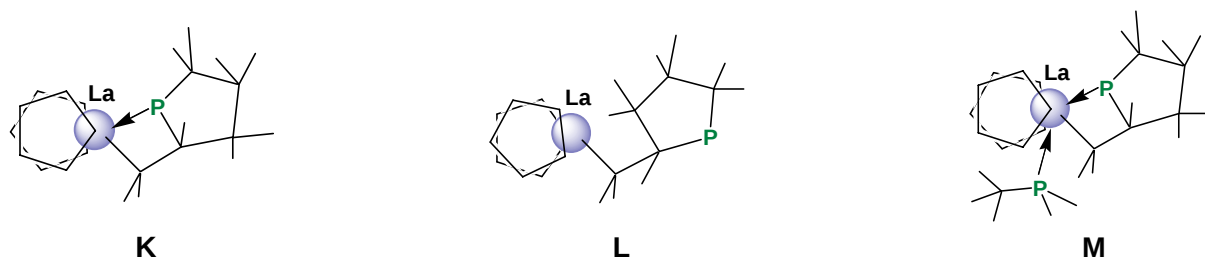


Conformation **H** involves coordination of the cyclized amine and is computed to be ~16.4 kcal/mol more stable than conformation **I**, whereas intermolecular coordination of free amine (using methylamine as a model) accrues an additional ~18 kcal/mol stabilization for amine-amido complex **J** vs. structure **I**. Thus, these calculations suggest that the monoinsertion products **F** and **G** are likely stabilized by the intramolecular amine coordination to the electrophilic lanthanide center.

DFT/B3LYP level analysis of the functionally analogous organolanthanide-catalyzed hydrophosphination/cyclization of 1-phosphinopent-4-ene (eq 4-7) reveals both distinct differences and similarities between N and P.<sup>25</sup> Interestingly, geometry optimizations of the

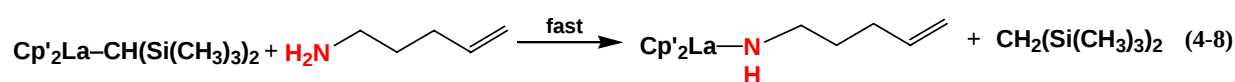


phosphine cyclization products also reveal two stable conformations (**K** and **L**), similar to the aforementioned hydroamination results.<sup>25</sup> Conformation **K** involves P-coordination of cyclized phosphine to the La center and is computed to be 13.1 kcal/mol more stable than conformation **L**, and again coordination of free phosphine (using methylphosphine as a model) results in a phosphine-phosphido complex with additional ~7 kcal/mol stabilization (**M**) versus **L**. As a

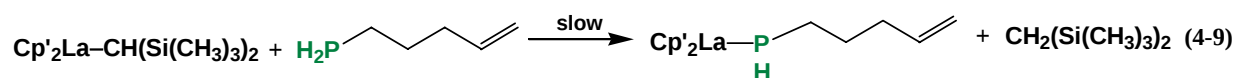


likely consequence of this intramolecular heteroatom coordination, the present systems implementing di-*sec*-butyl- and *N,N*-bis(trimethylsilyl)amine most frequently afford monoinsertion products.

*Step iii.* Theoretical and experimental evidence both indicate rapid, quantitative protonolysis of the Ln-alkyl precatalyst with amines (eq 4-8, Figure 4-9) in contrast to more sluggish protonolysis with analogous phosphines (eq 4-9, Figure 4-9).<sup>8,18</sup> Invoking hard/soft



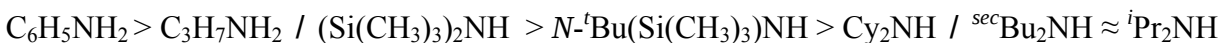
acid-base concepts, these differences in protonolysis rates may reflect the “softer” nature of P versus N,<sup>26</sup> despite the stronger Brønsted acidity of  $\text{R}_2\text{PH}$  versus  $\text{R}_2\text{NH}$ .<sup>27</sup> Thus, the



experimental and theoretical results argue that alkene insertion is turnover-limiting for hydroamination and that Ln-C bond protonolysis is turnover-limiting for hydrophosphination, in excellent agreement with the more facile chain growth observed in the phosphine polymerization/chain-transfer systems.<sup>8</sup>

The rate of protonolytic Ln-C bond cleavage is likely governed by both the steric bulk and the Brønsted acidity of the amine reagent (Scheme 4-3, step *iii*). The experimental solution-

phase Brønsted acidity of the amine chain-transfer agents investigated here decreases in the order:<sup>28</sup>

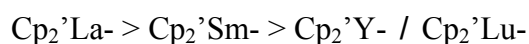


As noted above, the overall  $M_n$  of the product polymers reflects the rates governing chain growth in Scheme 3, steps *i* and *ii* ( $k^{\text{ethylene}}$ ) counterbalanced by the rate of competing Scheme 4-3, step *iii* protonolysis ( $k^{\text{NH}}$ ). Thus, di-*iso*-propyl- and *N-tert*-butyl(trimethylsilyl)amine are moderately efficient protonolytic chain-transfer agents for  $\text{Cp}'_2\text{La}$ -mediated systems and produce amine-capped oligoethylenes in reasonable yields (rates *i/ii* > rate *iii*, Scheme 4-3). However, only when the appropriate balance of steric and electronic properties is achieved can efficient chain propagation occur before chain-growth termination (rates *i/ii* >> rate *iii*, Scheme 4-3), such as in the case of dicyclohexylamine (Table 4-1). Lanthanocene-mediated (La, Sm) ethylene polymerizations in the presence of dicyclohexylamine result in high molecular weight polyethylenes, likely reflecting the increased amine steric bulk and decreased secondary amine Brønsted acidity. This plausibly suggests that steric repulsions in monoinsertion products **N** and **O** may render intramolecular or intermolecular amine coordination less favorable versus the other amines investigated. The  $\text{Cp}'_2\text{La}$ - and  $\text{Cp}'_2\text{Sm}$ - catalysts produce dicyclohexylamine-terminated polyethylenes with productivities as high as  $10^4$  g polymer/(mol Ln•atm ethylene•h), whereas  $\text{Cp}'_2\text{Y}$ - and  $\text{Cp}'_2\text{Lu}$ -mediated systems are less efficient, producing only trace amounts of polymer with productivities of  $10^2$  g polymer/(mol Ln•atm ethylene•h), reflecting known trends in  $\text{Cp}'_2\text{Ln-NR}_2$  olefin insertion reactivity with falling ionic radius (see more below).<sup>19</sup>



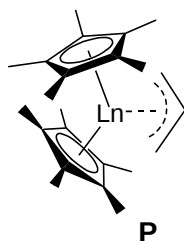
The organotitanium-mediated ethylene and propylene homopolymerizations conducted here in the presence of secondary amines result in small quantities of product polymers, likely reflecting the relative inertness of the  $\text{Ti}^+-\text{NR}_2$  bond and/or the greater stability of structures such as **O** for cationic  $d^0$  centers.<sup>23b</sup> The addition of dicyclohexylamine to the Ti-mediated systems allows rapid C=C propagation prior to chain termination with productivities up to  $10^4$  g polymer/(mol Ti $\cdot$ atm monomer $\cdot$ h), likely a consequence of slow chain-transfer for this sterically encumbered amine. The addition of less bulky di-*iso*-propylamine results in no detectable insertion products, presumably due to slow C=C insertion. The rates of propagation of higher  $\alpha$ -olefins, such as 1-hexene, are too slow ( $k_p^{\text{1-hexene}} \ll k_p^{\text{ethylene}}$ ) to effect sufficient chain growth, resulting in no detectable insertion products. Thus, organotitanium-mediated polymerization systems are capable of producing amine-functionalized polyolefins albeit currently with limited scope and efficiency versus organolanthanide systems.

**Effect of Lanthanide Ionic Radius on Chain Transfer Reactivity.** The present lanthanide ionic radius-polymerization activity trend parallels that for small-molecule hydroamination<sup>19</sup> and ethylene homopolymerization<sup>15</sup> (Table 4-1, entries 1-4):



This trend indicates more facile C=C enchainment in the coordination spheres of larger lanthanide ions ( $\text{La}^{+3}$ ,  $\text{Sm}^{+3}$ )<sup>15</sup> and also steric constraints around the smaller ions ( $\text{Y}^{+3}$ ,  $\text{Lu}^{+3}$ ).

Interestingly, larger  $\text{La}^{+3}$  produces slightly lower molecular weight polymeric products versus those produced with  $\text{Sm}^{+3}$ , likely reflecting the sensitive steric demands and competition between ethylene insertion/propagation ( $k_p^{\text{ethylene}}$ ) versus protonolytic amine chain transfer ( $k_t^{\text{NH}}$ ; Table 4-1, entries 3 and 4). Thus, larger  $\text{La}^{3+}$  mediates somewhat more rapid ethylene propagation versus the smaller  $\text{Sm}^{3+}$  ion,  $k_p^{\text{ethylene}}(\text{La}^{3+}) > k_p^{\text{ethylene}}(\text{Sm}^{3+})$  but also slightly more rapid amine protonolytic chain-transfer,  $k_t^{\text{NH}}(\text{La}^{3+}) > k_t^{\text{NH}}(\text{Sm}^{3+})$ . Regardless of lanthanide ion, propylene homopolymerizations in the presence of dicyclohexylamine afford no detectable olefin insertion products. One possible explanation lies in facile documented organolanthanide-mediated propylene C-H activation processes.<sup>10,15,17,29</sup> This would reduce the efficiency of  $\alpha$ -olefin polymerization for monomers such as propylene, where chain termination by substrate allylic C-H activation results in inactive/less polymerization active  $\eta^3$ -allyl species (**P**).<sup>29</sup>



That 1-hexene homopolymerizations mediated by  $\text{Cp}'_2\text{LnNCy}_2$  complexes in the presence of amines also afford no detectable insertion products is presumably due to unfavorable C-H activation processes (vide supra) or sluggish insertion rates for the more sterically encumbered monomer.

**Kinetics and Mechanism of Organolanthanide-Catalyzed Amine Chain-Transfer Processes.** The catalytic system  $\text{Cp}'_2\text{LaNCy}_2 + \text{HNCy}_2 + \text{ethylene}$  produces dicyclohexylamine-capped polyethylenes over a wide range of amine concentrations (Table 4-1, entries 5-9). A

series of polymerizations with varying dicyclohexylamine concentrations (in pseudo-zero-order excess) was conducted using  $\text{Cp}'_2\text{LaNCy}_2$  as the catalyst and with constant catalyst and ethylene concentrations and rapid mixing. Under these conditions, a linear relationship between  $M_n$  and  $[\text{dicyclohexylamine}]^{-1}$  is observed (Figure 4-3), consistent with amine chain termination being the dominant chain termination pathway. The absence of vinyl resonances in the product polymer  $^1\text{H}$  NMR spectrum and the  $\sim 1 : 1$   $-\text{CH}_3 : -\text{CH}_2\text{N}$  chain end ratio also supports amine chain transfer as the dominant chain-transfer pathway (Figure 4-1, Scheme 4-3). Under steady-state conditions, the number-average degree of polymerization,  $P_n$ , is equal to the sum of all rates of propagation,  $\Sigma R_p$ , divided by the rates of all competing chain-transfer pathways,  $\Sigma R_t$  (eq 4-10).<sup>30</sup> Assuming a single dominant chain-transfer process by amine protonolysis and rapid chain reinitiation after chain transfer,  $P_n$  is given by eq 4-11, where  $k_p$  is the rate constant for propagation and  $k_t^{\text{NH}}$  is the rate constant for intermolecular amine chain-transfer.

$$\overline{P}_n = \frac{\Sigma R_p}{\Sigma R_t} \quad (4-10)$$

$$\overline{P}_n = \frac{k_p^{\text{ethylene}} [\text{ethylene}]}{k_t^{\text{NH}} [\text{amine}]} \quad (4-11)$$

With polymerizations carried out at constant catalyst and monomer concentrations and with a pseudo-zero-order excess in dicyclohexylamine concentration, Figure 4-3 shows that eq 4-11 is obeyed over a broad amine concentration range. Using this equation and the data in Figure 4-3 yields rate constant ratios for La-mediated polymerizations, where the  $k_p^{\text{ethylene}}/k_t^{\text{NH}}$  rate constant ratio is  $\gg 1$ , thus indicating that chain propagation is very rapid versus amine chain-transfer. For the present system  $k_p^{\text{ethylene}}/k_t^{\text{NH}} \approx 1700$ , approximately 10 x the ratios observed for

$\text{Cp}'_2\text{YPPH}_2$ - ( $k_p^{\text{ethylene}}/k_{\text{phosphine}} \approx 200$ , diphenylphosphine),<sup>8a</sup>  $[\text{Cp}'_2\text{SmH}]_2$ - ( $k_p^{\text{ethylene}}/k_{\text{Si}} \approx 190$ , phenylsilane),<sup>5e</sup> and  $\text{CGCTiMe}_2/\text{PhC}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -mediated ( $k_p^{\text{ethylene}}/k_{\text{Si}} \approx 180$ , 5-hexenylsilane)<sup>5a,c</sup> polymerization systems. The present large  $k_p^{\text{ethylene}}/k_t^{\text{NH}}$  ratio is consistent with the exceptionally high product polymer molecular weights, which are  $\sim 10 \times$  those reported in the aforementioned systems using phosphines and silanes as chain-transfer agents at approximately the same concentrations. In the present systems, product high molecular weights are similar to those produced in the absence of the chain-transfer agent.<sup>15</sup> The single-site character of the present polymerization system is completely consistent the aforementioned good polymerization activities, high product molecular weights, and narrow polydispersities ( $M_w/M_n \approx 2.0$ ), further supporting the protonolytic amine chain-transfer scenario of Scheme 4-3.

## Conclusions

This investigation demonstrates that amines can act as efficient Ln-C cleaving/C-N bond-forming chain-transfer agents in  $\text{Cp}'_2\text{Ln}$ -mediated ethylene polymerization systems. The overall efficiency of amine chain-transfer processes in lanthanocene-mediated ethylene polymerizations increases in the order:

$\text{C}_6\text{H}_5\text{NH}_2 \approx \text{C}_3\text{H}_7\text{NH}_2 \ll (\text{Si}(\text{CH}_3)_3)_2\text{NH} \approx {}^{\text{sec}}\text{Bu}_2\text{NH} < N\text{-}^t\text{Bu}(\text{Si}(\text{CH}_3)_3)\text{NH} \approx {}^i\text{Pr}_2\text{NH} < \text{Cy}_2\text{NH}$

Primary amines are least efficient and do not yield insertion products, likely due to strong amine/amide binding to the  $\text{Ln}^{+3}$  center and the high resulting olefin insertion barrier. Among secondary amines, *N,N*-bis(trimethylsilyl)amine and di-*sec*-butylamine are the least efficient chain-transfer agents, producing only mono-ethylene insertion products. *N-tert*-butyl(trimethylsilyl)amine and di-*iso*-propylamine are also efficient chain-transfer agents for  $\text{Cp}'_2\text{La}$ -mediated polymerizations, producing oligoethylene products. Dicyclohexylamine is the

most effective chain-transfer agent found for lanthanocene-mediated ethylene polymerizations, producing high molecular weight linear, chain-end functionalized polymeric products. Organotitanium-mediated olefin polymerizations in the presence of secondary amines produce small amounts of functionalized polymer products with limited scope and efficiency compared to the lanthanocene-mediated systems.

A series of  $\text{Cp}'_2\text{LaCy}_2$ -mediated polymerizations with varying amine concentrations was carried out and revealed good polymerization rates, high product polymer molecular weights,  $M_w/M_n \approx 2.0$ , negligible  $\beta$ -hydride elimination NMR resonances, a 1 : 1 ratio of  $\text{CH}_3$  :  $\text{CH}_2\text{N}$  chain end units, and a linear relationship between  $M_n$  and  $[\text{dicyclohexylamine}]^{-1}$ , all consistent with a predominant protonolytic, amine chain-transfer mechanism. Due to the complex interplay of insertion, propagation, and protonolysis rates, careful optimization of amine steric and electronic properties is necessary to afford high molecular weight heteroatom-functionalized polymers. We have shown here that lanthanocene-catalyzed hydroamination and ethylene polymerization can be coupled in a catalytic cycle to produce amine-terminated polyethylenes and oligoethylenes with good activities and narrow polydispersities. Thus, the addition of amines to organo- $\text{f}^n, \text{d}^0$ -single-site-mediated ethylene polymerization systems is an effective, versatile method for incorporating reactive functional groups into an otherwise inert polyolefin.

## REFERENCES AND NOTES

## Chapter 1

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