

Silicon-Modified Ziegler–Natta Polymerization. Catalytic Approaches to Silyl-Capped and Silyl-Linked Polyolefins Using “Single-Site” Cationic Ziegler–Natta Catalysts

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Abstract: This contribution reports efficient and selective organotitanium-mediated silanolytic (PhSiH_3 , PhMeSiH_2 , Me_2SiH_2 , Et_2SiH_2) chain transfer in the homogeneous polymerization and copolymerization of a variety of α -olefins. The result is several broad classes of silyl-capped and silyl-linked polyolefins which have been characterized by $^1\text{H}/^{13}\text{C}/^{29}\text{Si}$ NMR and IR spectroscopy as well as by GPC. “Single-site” Ziegler–Natta catalysts effect this chain transfer with significant efficiency and scope. For $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)\text{BuN}]\text{TiMe}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -mediated propylene polymerization, the mechanism of chain transfer is supported by the observation that M_n of the capped atactic polypropylenes produced at constant [catalyst], $[\text{PhSiH}_3]$, and [propylene] is inversely proportional to $[\text{PhSiH}_3]$. Using the same catalyst, this process also efficiently produces silyl endcapped poly(1-hexene), ethylene + 1-hexene copolymers, ethylene + styrene copolymers (both with high degrees of comonomer incorporation), and (at low temperatures) polyethylene. In the case of *rac*- $\text{C}_2\text{H}_4(\text{Ind})_2\text{TiMe}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ + propylene and $(\text{Me}_5\text{C}_5)\text{TiMe}_2^+\text{B}(\text{C}_6\text{F}_5)_4^-$ + styrene, PhH_2Si -functionalized isotactic polypropylene and syndiotactic polystyrene, respectively, are produced. Using 1,4-disilabenzene and 1,3,5-trisilabenzene as chain-transfer agents in the presence of $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)\text{BuN}]\text{TiMe}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ + propylene, linear diblock and starlike atactic polypropylene structures, respectively, are produced. In addition to primary silanes, secondary silanes (PhMeSiH_2 , Me_2SiH_2 , Et_2SiH_2) are efficient and selective chain-transfer agents in this organotitanium-mediated polymerization. In the presence of $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)\text{BuN}]\text{TiMe}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ + propylene, $(\text{Me}_5\text{C}_5)\text{TiMe}_2^+\text{B}(\text{C}_6\text{F}_5)_4^-$ + propylene, and $(\text{Me}_5\text{C}_5)\text{TiMe}_2^+\text{B}(\text{C}_6\text{F}_5)_4^-$ + styrene, PhMeHSi - or Me_2HSi -capped atactic polypropylene and PhMeHSi -, Me_2HSi -, or Et_2HSi -capped syndiotactic polystyrene are produced, respectively. Using PhH_2Si -capped polypropylene as a chain-transfer agent, an atactic polypropylene–syndiotactic polystyrene AB block copolymer is produced in the presence of $(\text{Me}_5\text{C}_5)\text{TiMe}_2^+\text{B}(\text{C}_6\text{F}_5)_4^-$ + styrene.

Introduction

Although polyolefins have numerous applications,¹ the utility of these versatile macromolecules is significantly limited by their chemical inertness. This characteristic results in less than optimum chemical and physical properties in regard to compatibility with polar materials, i.e., limited adhesion, paintability, barrier characteristics, biocompatibility, etc. These deficiencies could, in principle, be overcome by controlled introduction of appropriate polar or reactive functional groups, a useful and general method for modifying macromolecule chemical and physical properties.^{1–5} In addition to promoting the aforementioned desirable properties, such functional sites offer precursors

for constructing diverse block or graft copolymer structures. Current routes to functionalized polyolefins include (i) partial chemical modification of preformed polyolefins,^{2c,3b,6} (ii) free radical graft polymerization,^{1e,7} (iii) polymerization of alkenes with polar comonomers,⁸ (iv) monomer modification,^{2,3} and (v) chain transfer to organometalloids (MR_n , $\text{M} = \text{Zn}, \text{Al}, \text{etc.}$).⁵ Nevertheless, although important progress has been made in this area, the *selective and catalytic in situ introduction* of

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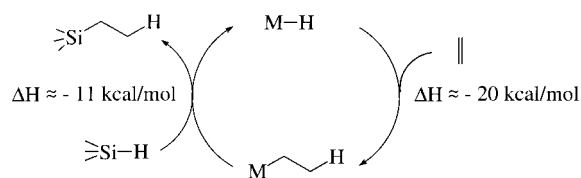
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Scheme 1



functional moieties into the structures of polyolefins is currently a significant, incompletely addressed challenge.⁹

In addition to the introduction of appropriately reactive functional groups, efficient control of molecular weight is a central issue in contemporary polymer synthesis. The most general means to control molecular weight is via chain-transfer processes which cleanly terminate chain growth in situ. A number of chain-transfer processes,^{1c,5,10} including β -H elimination, β -alkyl elimination, chain transfer to monomer, chain transfer to aluminum, and hydrogenolysis, have been identified for Ziegler–Natta olefin polymerization processes.¹ Synthetically, hydrogenolysis is arguably the most attractive since it is readily implemented, generally displays well-behaved kinetics, and is normally not detrimental to catalyst activity. However, there are cases in which hydrogen is not optimum due to undesired side effects (e.g., unresponsive M–R bonds, over-activation of the catalyst, too rapid hydrogenation of other functional groups, etc.). Efficient, alternative chain-transfer processes are presently limited and frequently nonselective as in situ chain termination routes. Therefore, discovering and understanding new chain-transfer processes for use in the catalytic synthesis of olefin homopolymers and copolymers would be highly desirable.

In regard to metal–ligand enthalpy aspects of metallocene-mediated polymerization and chain transfer, insertion of olefins into lanthanide or early transition metal hydride bonds is estimated to be generally exothermic,^{1,11,12} while processes such as M–C/Si–H transposition are also estimated to be exothermic^{11,12} (Scheme 1). From these considerations and the robust yet chemically versatile character of organosilanes, silane derivatives represent attractive yet relatively unexplored^{13,14} chain-transfer agents for α -olefin polymerization processes. We

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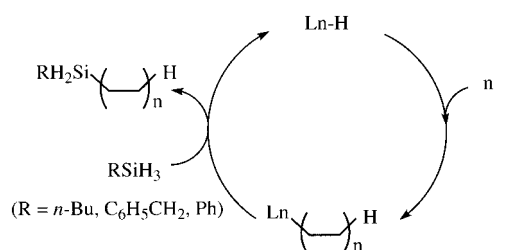
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Scheme 2



previously reported that silyl-capped polyethylene and silyl-capped ethylene copolymers^{13,14} can be efficiently produced in the presence of PhSiH_3 via an *organolanthanide-mediated* catalytic cycle (Scheme 2).¹³ It was demonstrated that polymer molecular weight can be modulated by varying PhSiH_3 concentration and that the silyl group is selectively delivered to a single terminus of the polymer chain in a process regiochemically distinct from that expected in catalytic hydrosilylation¹⁵ of a polymeric β -hydride elimination/chain transfer to monomer product. Once formed, the silicon–carbon bond is a versatile precursor of a myriad of polar and nonpolar functional groups and linkers.¹⁶

These observations raise intriguing questions concerning the scope of silanes useful as polyolefin chain-transfer agents, whether this chain-transfer process can be effected by more conventional group 4 catalysts,^{1–5} whether the scope can be extended beyond simple ethylene-based polymers, whether this chain-transfer process can be extended to stereospecific α -olefin homopolymerizations, and whether this chain-transfer process can lead to more elaborate polymer architectures using silicon as a linker. We present here a full account of efficient and selective organotitanium-mediated silanolytic chain transfer in the homogeneous polymerization and copolymerization of a variety of α -olefins, yielding broad classes of new linear, stereoregular, and unusual branched silapolyolefins, which have been characterized by $^1\text{H}/^{13}\text{C}/^{29}\text{Si}$ NMR and infrared spectroscopy and by GPC.¹⁷

Experimental Section

Materials and Methods. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line, or interfaced to a high-vacuum (10^{-5} Torr) line, or in a nitrogen-filled Vacuum Atmospheres glovebox with a high-capacity recirculator (<1 ppm O_2). Argon, ethylene, and propylene (Matheson, prepurified) were purified by passage through a MnO oxygen removal column and a Davison 4-A molecular sieve column. Hydrocarbon solvents (toluene, *n*-pentane, *n*-heptane) were distilled under nitrogen from Na/K alloy.

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All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy in resealable bulbs. Other olefins (styrene, 1-hexene) were obtained from Aldrich, stirred over CaH₂ for 24 h, and vacuum transferred. Phenylsilane was obtained commercially (Aldrich), dried over CaH₂ for 24 h, and distilled prior to use. The reagents 1,4-disilabenzene¹⁸ and 1,3,5-trisilabenzene¹⁸ were prepared according to literature procedures. Et₂SiH₂ was obtained commercially (Gelest), dried over CaH₂ for 24 h, and distilled prior to use. Me₂SiH₂ was obtained commercially (Gelest) and purified by passage through a MnO/SiO₂ column prior to use. Ph₃C⁺B(C₆F₅)₄⁻ was obtained commercially (Asahi Glass) and was used without further purification. The organolanthanide and organotitanium catalysts, Me₂Si(Me₄C₅)SmCH(SiMe₃)₂,¹⁹ [Me₂Si(Me₄C₅)(BuN)]TiMe₂,²⁰ (Me₄C₅)TiMe₃,²¹ and *rac*-C₂H₄(Ind)₂TiMe₂,²² were prepared according to published procedures.

Physical and Analytical Measurements. NMR spectra were recorded on either Varian VXR 300 (FT, 300 MHz, ¹H; 75 MHz, ¹³C) or UNITYplus 400 (FT, 400 MHz, ¹H; 100 MHz, ¹³C; 79.5 MHz, ²⁹-Si) instruments. Chemical shifts for ¹H and ¹³C spectra were referenced to internal solvent resonances and are reported relative to tetramethylsilane. ²⁹Si NMR spectra were referenced to external tetramethylsilane. NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed tubes (J. Young). For ¹³C NMR analyses of homopolymer microstructures, 40–60 mg polymer samples were dissolved in 0.7 mL of C₂D₂Cl₄ with a heat gun in a 5 mm NMR tube, and the samples were immediately transferred to the NMR spectrometer with probehead preequilibrated at 120 °C. A 45° pulse width and 2.5 s acquisition time were used with a pulse delay of 5 s. For ¹³C NMR analyses of copolymer microstructures, the samples were prepared by dissolving 50 mg polymer samples in 0.7 mL of C₂D₂Cl₄, and spectra were taken at 120 °C with a 10-s pulse delay and a 90° pulse width. 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 at Dow Corning Corp. (Midland, MI) relative to polystyrene standards, except in the case of R₂SiH-capped polyolefins, which were calibrated with a Universal Calibration Curve. IR spectra were recorded on KBr pellets using a Nicolet 520 FT-IR spectrometer with an MCT detector.

PhH₂Si-Capped Polypropylene. Representative Experiment. On the vacuum line, toluene (50 mL) was condensed into a flamed, 250 mL reaction flask equipped with a large magnetic stirring bar and a septum-covered sidearm. Next, 0.30 mL (2.4 mmol) of PhSiH₃ was vacuum transferred into the flask at -78 °C. In the glovebox, a 6 mL sample vial equipped with a septum cap was charged with 10 mg (0.031 mmol) of [Me₂Si(Me₄C₅)(BuN)]TiMe₂ and 28 mg (0.030 mmol) of Ph₃C⁺B(C₆F₅)₄⁻. A measured amount of toluene (2 mL) was then syringed into the vial with a dry, Ar-purged gastight syringe. The vial was then removed from the glovebox immediately prior to the polymerization experiment, and the catalyst solution was syringed through the septum-sealed sidearm into the rapidly stirring reaction flask under 1.0 atm of propylene. After a measured time interval, the reaction was quenched by addition of 2.0 mL of methanol. The polymer was collected by filtration and then extracted with *n*-pentane (50 mL). The polymer was isolated after filtration by evaporating the solvent to dryness and washing the product with methanol and acetone, followed by drying under vacuum. Yield, 2.5 g. *M_n* = 24 000, *M_w* = 41 100 by GPC. ¹H NMR (C₆D₆, relative intensity): δ 7.50 (*Ph*, 0.4), 7.20 (*Ph*, 0.4), 4.48 (*SiH₂*, 0.4), 1.74 (*-CH-*, 33), 1.21 (*-CH₂-*, 66), 0.96 (*-CH₃*, 100), 0.78 (*-CH₂-*, 0.4). ¹³C NMR (C₆D₆, 75.5 MHz): δ 136.2, 130.1, 129.8, 128.7, 47.4, 47.1, 46.7, 46.3, 45.9, 44.8, 32.3, 29.5, 27.8, 23.1, 21.3, 20.9, 20.6, 20.4, 20.0, 19.6, 14.5, 1.95.

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Synthesis of an Authentic PhSiH₂-Capped Polypropylene Sample. Representative Hydrosilylation Experiment. In glovebox, 50 mg of vinylidene-terminated polypropylene (*M_n* = 4400)²³ and 20 μL (0.15 mmol) of PhSiH₃ were charged successively into a J-Young NMR tube equipped with a Teflon valve (previously flamed in vacuo). Next, 3 mg (5 μmol) of Me₂Si(Me₄C₅)₂SmCH(SiMe₃)₂ was dissolved in 0.7 mL of C₆D₆, and the resulting solution was transferred into the NMR tube containing the polymer and silane. The NMR tube was removed from glovebox and maintained at 60 °C. After 12 h, 95% of the vinylidene-terminated polypropylene was converted to silyl-capped polypropylene. The NMR data are identical to those for the above chain-transfer reaction product.

Polymerization of Propylene in the Presence of 1,4-Disilabenzene. Representative Experiment. On the vacuum line, toluene (50 mL) was condensed into a flamed, 250 mL reaction flask equipped with a large magnetic stirring bar and a septum-covered sidearm. Next, 0.07 mL (0.46 mmol) of 1,4-disilabenzene was added to the flask via syringe under an Ar counterflow at -78 °C. In the glovebox, a 6 mL sample vial equipped with a septum cap was loaded with 17 mg (0.052 mmol) of [Me₂Si(Me₄C₅)(BuN)]TiMe₂ and 48 mg (0.052 mmol) of Ph₃C⁺B(C₆F₅)₄⁻. A measured amount of toluene (2 mL) was then syringed into the vial with a dry, Ar-purged gastight syringe. The vial was removed from the glovebox immediately prior to the polymerization experiment, and the catalyst solution was syringed through the septum-sealed sidearm under an Ar counterflow into the rapidly stirring reaction flask attached to the high-vacuum line at -78 °C. The reaction flask was then evacuated, and a measured pressure of propylene (0.11 atm) was introduced into the reaction vessel. The propylene pressure was then slowly decreased (using a mercury U-tube manometer) to parallel the calculated decrease in 1,4-disilabenzene concentration as the polymerization proceeded. It required 4 h to consume the 1,4-disilabenzene, and the reaction mixture was stirred an additional 10 h. The reaction was next quenched by addition of 2.0 mL of methanol, and the polymer wax collected by filtration and then extracted with *n*-pentane (50 mL). The polymer was isolated by filtration, the filtrate evaporated to dryness, and the product washed with methanol and acetone, followed by drying under vacuum. Yield, 1.8 g. *M_n* = 5400, *M_w* = 23 000 by GPC. ¹H NMR (C₆D₆, relative intensity): δ 7.50 (*Ph*, 0.4), 4.52 (*SiH₂*, 0.4), 1.74 (*-CH-*, 33), 1.21 (*-CH₂-*, 66), 0.96 (*-CH₃*, 100), 0.78 (*-CH₂-*, 0.4). ¹³C NMR (C₆D₆, 75.5 MHz): δ 136.0, 129.5, 129.0, 125.4, 47.2, 47.1, 46.7, 46.4, 46.2, 46.0, 40.6, 30.2, 27.8, 25.5, 23.6, 22.7, 20.6, 20.4, 20.1, 19.9, 19.7, 14.7. ²⁹Si MNR (C₆D₆, 79.5 MHz): δ -34.0.

Polymerization of Propylene in the Presence of 1,3,5-Trisilabenzene. The same procedure as for the above reaction was employed, except that 1,3,5-trisilabenzene was used as the chain-transfer agent (0.070 mL, 0.42 mmol). Yield, 2.1 g. *M_n* = 7400, *M_w* = 64 600 by GPC. ¹H NMR (C₆D₆, relative intensity): δ 7.90 (*Ph*, 0.17), 4.55 (*SiH₂*, 0.33), 1.74 (*-CH-*, 31), 1.18 (*-CH₂-*, 63), 1.03 (*-CH₃*, 100), 0.80 (*-CH₂-*, 0.09). ¹³C NMR (C₆D₆, 75.5 MHz): δ 143.6, 132.5, 47.9, 47.3, 46.8, 46.4, 46.0, 45.2, 40.6, 30.2, 27.9, 27.8, 25.5, 23.6, 22.7, 20.6, 20.2, 20.1, 19.9, 19.7, 14.7. ²⁹Si MNR (C₆D₆, 79.5 MHz): δ -33.7.

Oxidative C–Si Cleavage of Atactic Polypropylene-Functionalized 1,3,5-Trisilabenzene. A 100 mL three-neck flask with an addition funnel and reflux condenser was charged with the atactic polypropylene functionalized trisilabenzene (1 g, dissolved in 5 mL of *n*-hexane) and CF₃COOH (5.0 g, 42 mmol). The resulting solution was heated to 50 °C and allowed to stir for 5 h. The volatiles were then removed under reduced pressure, and 5 mL of *n*-hexane was introduced into the residue. Next, MeOH (0.76 g, 21 mmol) and KHF₂ (1.17 g, 15 mmol) were added to the *n*-hexane solution, and the mixture was stirred at 50 °C. With stirring, 0.61 g (20 mmol) of NaHCO₃, 1.5 g (45 mmol) of a 30% H₂O₂ solution, 20 mL of MeOH, and 20 mL of THF were then added, and the mixture was refluxed for 48 h. The reaction was next quenched with a dilute solution of NaHSO₃ (20 mL) at 0 °C and extracted with diethyl ether, and the ether extract was dried under high

(23) The vinylidene-terminated polypropylene was produced by the same procedure as for the PhH₂Si-capped polypropylene, except that silane was not introduced and [Me₂Si(Me₄C₅)³BuN]ZrMe₂ was used as the precatalyst. *M_n* = 4400 by ¹H NMR. ¹H NMR (C₆D₆): δ 4.82 ppm (doublet, vinylidene end group).

vacuum. Yield, 0.53 g (53%) of HO-capped polypropylene. $M_n = 3300$, $M_w = 25\ 000$. IR (neat): $\nu_{\text{O-H}} = 3350\ \text{cm}^{-1}$.

PhSiH₂-Capped Poly(1-hexene). Representative Experiment. In the glovebox, 10 mg (0.031 mmol) of $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(t\text{-BuN})]\text{TiMe}_2$ and 28 mg (0.030 mmol) of $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ were loaded into a 100 mL round-bottom flask equipped with a large magnetic stirring bar. On the vacuum line, 10 mL of toluene was added to the flask via syringe under an Ar counterflow. After evacuation, 0.40 mL (3.0 mmol) of PhSiH_3 and 7.5 mL (0.060 mol) of 1-hexene were then vacuum transferred into the flask at $-78\ ^\circ\text{C}$. The mixture was next warmed to $25\ ^\circ\text{C}$ while being stirred rapidly for 60 min, and the reaction was then quenched by addition of 2.0 mL of methanol. The polymeric product was collected by filtration and then extracted with *n*-hexane (50 mL). The polymer was isolated by filtration, the solvent evaporated, and the product washed with methanol and acetone, followed by drying under vacuum. Yield, 3.1 g. $M_n = 2500$, $M_w = 6200$ by GPC. ^1H NMR (C_6D_6 , relative intensity): δ 7.50 (*Ph*, 0.2), 7.20 (*Ph*, 0.2), 4.48 (*SiH*₂, 0.2), 1.65 ($-\text{CH}-$, 9.6), 1.46 ($-\text{CH}_2-$, 100), 1.13 ($-\text{CH}_3$, 39). ^{13}C NMR (C_6D_6 , 75.5 MHz): δ 136.5, 136.2, 135.5, 129.6, 46.0, 45.6, 40.9, 35.7, 34.6, 32.9, 32.4, 29.2, 27.2, 25.1, 23.8, 23.4, 17.5, 16.9, 16.8, 14.5, 14.4, 10.4.

Ethylene + Styrene Copolymerization. Representative Experiment. In the glovebox, 10 mg (0.031 mmol) of $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(t\text{-BuN})]\text{TiMe}_2$ and 28 mg (0.030 mmol) of $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ were loaded into a 100 mL round-bottom flask equipped with a large magnetic stirring bar. On the vacuum line, 10 mL of toluene was added to the flask via syringe under an Ar counterflow. Next, 0.70 mL (5.0 mmol) of PhSiH_3 and 2.0 mL (0.017 mol) of styrene were vacuum transferred into the flask at $-78\ ^\circ\text{C}$. The mixture was warmed to $25\ ^\circ\text{C}$ and exposed to ethylene (1 atm) while being stirred rapidly for 60 min. The reaction was quenched by addition of 2.0 mL of methanol. The polymer was collected by filtration and then washed with methanol and acetone, followed by drying under high vacuum. Yield, 2.78 g. Polymer composition, 50% styrene incorporation by ^1H NMR. $M_n = 72\ 000$, $M_w = 100\ 000$ by GPC. ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, $120\ ^\circ\text{C}$, relative intensity): δ 7.70–6.95 (*Ph*, 90), 4.35 (*SiH*₂, 0.1), 2.80–2.30 ($-\text{CH}(\text{Ph})-$, 8.8), 1.70–1.40 ($-\text{CH}_2\text{CHPh}-$, 36), 1.40–0.90 ($-\text{CH}_2\text{CH}_2-$, 100). ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 75.5 MHz, $120\ ^\circ\text{C}$): δ 146.3, 145.8, 129.0, 128.0, 127.8, 127.6, 125.5, 41.0, 36.8, 34.3, 31.8, 29.6, 29.4, 27.5, 25.3, 24.2, 22.5, 13.7.

Ethylene + 1-Hexene Copolymerization. Representative Experiment. In the glovebox, 10 mg (0.031 mmol) of $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(t\text{-BuN})]\text{TiMe}_2$ and 28 mg (0.030 mmol) of $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ were loaded into a 100 mL round-bottom flask equipped with a large magnetic stirring bar. On the vacuum line, 10 mL of toluene was added to the flask via syringe under an Ar counterflow. After evacuation, 1.0 mL (6.0 mmol) of PhSiH_3 and 4.0 mL (0.032 mol) of 1-hexene were vacuum transferred into the flask at $-78\ ^\circ\text{C}$. The mixture was warmed to $25\ ^\circ\text{C}$ and exposed to ethylene (1 atm) while being stirred rapidly for 60 min. The reaction was then quenched by addition of 2.0 mL of methanol. The polymer was collected by filtration and then washed with methanol and acetone, followed by drying under high vacuum. Yield, 2.56 g. Polymer composition, 52% 1-hexene incorporation by ^1H NMR. $M_n = 50\ 000$, $M_w = 120\ 000$ by GPC. ^1H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, $120\ ^\circ\text{C}$, relative intensity): δ 7.50 (*Ph*, 0.07), 7.20 (*Ph*, 0.09), 4.49 (*SiH*₂, 0.07), 1.18 ($-\text{CH}-$, 8.4), 1.47 ($-\text{CH}_2\text{CH}_2-$, 100), 1.03 ($-\text{CH}_3$, 34). ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 75.5 MHz, $120\ ^\circ\text{C}$): δ 136.2, 131.2, 129.7, 126.9, 45.0, 40.9, 40.3, 39.4, 39.0, 37.9, 35.3, 34.8, 34.6, 34.3, 33.9, 32.9, 32.4, 31.9, 30.7, 30.2, 29.2, 27.1, 23.7, 23.1, 20.7, 15.6, 14.5.

Propylene + 1-Hexene Copolymerization. Representative Experiment. On a vacuum line, toluene (50 mL) was condensed into a flamed, 250 mL reaction flask equipped with a large magnetic stirring bar and a septum-covered sidearm. Next, 1.90 mL (11.4 mmol) of PhSiH_3 and 10 mL (0.080 mmol) of 1-hexene were vacuum transferred into the flask at $-78\ ^\circ\text{C}$. The mixture was warmed to $25\ ^\circ\text{C}$ and exposed to propylene (1 atm) while being stirred rapidly. In the glovebox, a 6 mL sample vial equipped with a septum cap was charged with 8 mg (0.024 mmol) of $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(t\text{-BuN})]\text{TiMe}_2$ and 19 mg (0.021 mmol) of $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$. A measured amount of toluene (2.0 mL) was then syringed into the vial with a dry, Ar-purged gastight syringe. The vial was removed from the glovebox immediately prior

to the polymerization experiment, and the solution was quickly syringed under a propylene counterflow into the rapidly stirred olefin + silane reaction mixture at $25\ ^\circ\text{C}$ through the septum-sealed reaction flask sidearm. After 30 min, the reaction was quenched by addition of 2.0 mL of methanol. The polymeric product was collected by filtration and then extracted with *n*-hexane (300 mL). The polymer was isolated by filtration, the filtrate evaporated, and the product washed with methanol and acetone, followed by drying under vacuum. Yield, 25 g. Polymer composition, 18% 1-hexene incorporation by ^1H NMR. $M_n = 10\ 600$, $M_w = 37\ 100$ by GPC. ^1H NMR (C_6D_6 , $25\ ^\circ\text{C}$, relative intensity): δ 7.50 (*Ph*, 0.2), 7.20 (*Ph*, 0.2), 4.52 (*SiH*₂, 0.2), 1.69 ($-\text{CH}-$, 31), 1.35 ($-\text{CH}_2-$, 36), 1.15 ($-\text{CH}_2-$, 34), 1.15 ($-\text{CH}_2-$, 43), 0.90 (*CH*₃, 100).

PhH₂Si-Capped Isotactic Polypropylene. Representative Experiment. In the glovebox, 10 mg (0.030 mmol) of *rac*- $\text{C}_2\text{H}_4(\text{Ind})_2\text{TiMe}_2$ and 24 mg (0.026 mmol) of $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ were loaded into a 100 mL round-bottom flask. On the vacuum line, 10 mL of toluene was added to the flask via syringe under an Ar counterflow. After evacuation, 1.0 mL (6.0 mmol) of PhSiH_3 was vacuum transferred into the flask at $-78\ ^\circ\text{C}$. The mixture was then warmed to $-45\ ^\circ\text{C}$ and exposed to propylene (1 atm) while being stirred rapidly for 10 min. The reaction was then quenched by addition of 2.0 mL of methanol, and the polymer was collected by filtration and washed with methanol, acetone, and *n*-hexane, followed by drying under high vacuum. Yield, 0.010 g. The isotacticity (*mmmm* pentad content) is >94% by ^{13}C NMR. $M_n = 8200$ by NMR. ^1H NMR (relative intensity, $\text{C}_2\text{D}_2\text{Cl}_4$, $120\ ^\circ\text{C}$): δ 7.52 (0.26, *Ph*), 7.35 (0.39, *Ph*), 4.22 (0.26, *SiH*₂), 1.62 (33, $-\text{CH}-$), 1.28 (66, $-\text{CH}_2-$), 0.88 (100, $-\text{CH}_3$). ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, $120\ ^\circ\text{C}$): δ 136.1, 128.2, 45.8, 28.2, 21.4, 16.2, 14.2.

PhH₂Si-Capped Syndiotactic Polystyrene. Representative Experiment. In the glovebox, 13 mg (0.057 mmol) of $(\text{Me}_3\text{C}_5)\text{TiMe}_3$ and 33 mg (0.036 mmol) of $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ were loaded into a 100 mL round-bottom flask. On the vacuum line, 10 mL of toluene was added to the flask via syringe under an Ar counterflow. The mixture was then warmed to $45\ ^\circ\text{C}$, and 1.0 mL (6.0 mmol) of PhSiH_3 + 5 mL of styrene were injected over 3 min via syringe with rapid stirring. The reaction was then quenched by addition of 2.0 mL of methanol. The polymer was collected by filtration and then washed with methanol and acetone, followed by drying under high vacuum. Yield, 4.48 g. The syndiotacticity is >98% by ^{13}C NMR. $M_n = 40\ 000$, $M_w = 84\ 000$ by GPC. ^1H NMR (relative intensity, $\text{C}_2\text{D}_2\text{Cl}_4$, $120\ ^\circ\text{C}$): δ 7.40–6.60 (100, *Ph*), 7.35 (66, *Ph*), 4.21 (0.26, *SiH*₂), 1.85 (33, $-\text{CH}-$), 1.35 (66, $-\text{CH}_2-$), 0.90 (0.39, $-\text{CH}_3$). ^{13}C NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 75.5 MHz, $120\ ^\circ\text{C}$): δ 145.2, 128.8, 128.0, 127.7, 127.6, 125.4, 40.8, 40.0, 21.5, 14.3. ^{29}Si NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 79.5 MHz): δ -29.0 .

PhMeHSi-Capped Atactic Polypropylene. On the high-vacuum line, toluene (20 mL) was condensed into a flamed, 100 mL reaction flask equipped with a large magnetic stirring bar and a septum-covered sidearm. Next, 1.50 mL (10.9 mmol) of PhMeSiH_2 was vacuum transferred into the flask at $-78\ ^\circ\text{C}$. The mixture was warmed to $25\ ^\circ\text{C}$ and exposed to propylene (1 atm) while being stirred rapidly. In the glovebox, a 6 mL sample vial equipped with a septum cap was charged with 10 mg (0.031 mmol) of $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(t\text{-BuN})]\text{TiMe}_2$ and 28 mg (0.030 mmol) of $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$. A measured amount of toluene (2.0 mL) was then syringed into the vial with a dry, Ar-purged gastight syringe. The vial was removed from the glovebox immediately prior to the polymerization experiment, and the catalyst solution was quickly syringed under a propylene counterflow into the rapidly stirred olefin + silane reaction mixture through the septum-sealed reaction flask sidearm at $25\ ^\circ\text{C}$. After 2 h, the reaction was quenched by addition of 2.0 mL of methanol. The polymeric product was collected by filtration and then extracted with *n*-pentane (50 mL). It was isolated by filtration, the filtrates evaporated, and the product washed with methanol and acetone, followed by drying under vacuum. Yield, 2.7 g. $M_n = 3300$, $M_w = 14\ 500$ by GPC. ^1H NMR (C_6D_6 , relative intensity): δ 7.48 (*Ph*, 0.28), 7.09 (*Ph*, 0.28), 4.60 (*SiH*, 0.14), 1.74 ($-\text{CH}-$, 32), 1.21 ($-\text{CH}_2-$, 68), 0.96 ($-\text{CH}_3$, 100), 0.78 ($-\text{CH}_2-$, 0.29), 0.44 (*CH*₃Si, 0.47). ^{29}Si NMR (C_6D_6 , 79.5 MHz): δ -2.0 .

PhMeHSi-Capped Syndiotactic Polystyrene. On the vacuum line, toluene (50 mL) was condensed into a flamed, 100 mL reaction flask equipped with a large magnetic stirring bar and a septum-covered

sidearm. Next, 1.0 mL (7.3 mmol) of PhMeSiH₂ and 1.5 mL of styrene were vacuum transferred into the flask at -78°C . In the glovebox, a 6 mL sample vial equipped with a septum cap was loaded with 10 mg (0.044 mmol) of (Me₅C₅)TiMe₃ and 28 mg (0.030 mmol) of Ph₃C⁺B(C₆F₅)₄⁻. A measured amount of toluene (2.0 mL) was then syringed into the vial with a dry, Ar-purged gastight syringe. The vial was removed from the glovebox immediately prior to the polymerization. The catalyst solution was quickly syringed under an Ar counterflow into the rapidly stirred olefin + silane reaction mixture at 120°C through the septum-sealed reaction flask sidearm. After 12 h, the reaction was quenched by addition of 2.0 mL of methanol. The polymeric product was collected by filtration and then washed with methanol and acetone, followed by drying under vacuum. Yield, 0.86 g. $M_n = 79\,500$, $M_w = 226\,100$ by GPC. ¹H NMR (relative intensity, C₂D₂Cl₄, 120°C): δ 7.40–6.60 (100, Ph), 6.35 (66, Ph), 1.85 (33, –CH–), 1.35 (66, –CH₂–), 0.90 (0.20, –CH₃), 0.82 (0.12, CH₃Si). The SiH resonance was not observed due to the high molecular weight of the polymer. IR (KBr): $\nu_{\text{Si-H}} = 2115\text{ cm}^{-1}$.

Me₂HSi-Capped Atactic Polypropylene. In the glovebox, 15 mg (0.066 mmol) of (Me₅C₅)TiMe₃ and 40 mg (0.043 mmol) of Ph₃C⁺B(C₆F₅)₄⁻ were loaded into a 100 mL round-bottom flask equipped with a large magnetic stirring bar. On the vacuum line, 30 mL of toluene was condensed into the flask. Next, 1.30 mL (14.7 mmol) of Me₂SiH₂ was vacuum transferred into the flask at -78°C , and 1 atm of propylene was introduced into the reaction flask with rapid stirring at -30°C . After 10 min, the reaction was quenched by addition of 2.0 mL of methanol. The polymeric product was collected by filtration and then extracted with *n*-hexane (50 mL). The polymer was isolated by filtration, the filtrate evaporated to dryness, and the product washed with methanol and acetone, followed by drying under vacuum. Yield, 1.6 g. $M_n = 36\,900$, $M_w = 157\,000$ by GPC. ¹H NMR (C₆D₆, relative intensity): δ 4.32 (SiH, 0.1), 3.98 (SiH, 0.1), 1.76 (–CH–, 31), 1.19 (–CH₂–, 60), 0.97 (–CH₃, 100), 0.15 (CH₃Si, 0.45), 0.05 (CH₃Si, 0.40). ¹³C NMR (C₆D₆, 75.5 MHz): δ 46.7, 46.0, 42.9, 35.5, 34.3, 27.8, 20.9, 20.6, 20.1, 19.9, 17.3, 15.1, 12.2, 11.8, 11.5, 5.2. ²⁹Si NMR (C₆D₆, 79.5 MHz): δ 5.4, 4.7.

Me₂HSi-Capped Syndiotactic Polystyrene. In the glovebox, 12 mg (0.053 mmol) of (Me₅C₅)TiMe₃ and 38 mg (0.041 mmol) of Ph₃C⁺B(C₆F₅)₄⁻ were loaded into a 100 mL round-bottom flask. On the vacuum line, 20 mL of toluene was condensed into the flask. Next, 1.0 mL of styrene was injected by syringe into the -78°C reaction flask. After evacuation, 3.0 mL (33.9 mmol) of Me₂SiH₂ was vacuum transferred into the rapidly stirred -78°C reaction mixture. The reaction mixture was then quickly warmed to 55°C with an oil bath. After 3 h, the reaction was quenched by addition of 2.0 mL of methanol. The polymeric product was collected by filtration and washed with methanol and acetone, followed by drying under high vacuum. Yield, 0.7 g. $M_n = 45\,000$ by ¹H NMR. ¹H NMR (relative intensity, C₂D₂Cl₄, 120°C): δ 7.40–6.80 (100, Ph), 6.35 (66, Ph), 4.24 (0.07, SiH), 1.85 (31, –CH–), 1.35 (65, –CH₂–), 0.90 (0.26, –CH₃), 0.52 (0.49, CH₃Si). ¹³C NMR (C₂D₂Cl₄, 75.5 MHz, 120°C): δ 145.2, 127.8, 127.6, 125.6, 43.5, 40.4, 33.3, 23.8, 22.6, 15.2, 14.2.

Me₂HSi-Capped Atactic Poly(1-hexene). In the glovebox, 13 mg (0.057 mmol) of (Me₅C₅)TiMe₃ and 30 mg (0.033 mmol) of Ph₃C⁺B(C₆F₅)₄⁻ were loaded into a 100 mL round-bottom flask. On the vacuum line, 20 mL of toluene was condensed into the flask. Next, 6.0 mL of 1-hexene was injected by syringe into the reaction flask. After evacuation, 2.0 mL (22.6 mmol) of Me₂SiH₂ was then vacuum transferred into the rapidly stirred reaction mixture at -78°C . The mixture was allowed to warm to 25°C . After 16 h, the reaction was then quenched by addition of 2.0 mL of methanol. The polymeric product was collected by filtration and washed with methanol and acetone, followed by drying under vacuum. Yield, 2.1 g of a mixture of uncapped and silyl-capped poly(1-hexene), in a 1:1 ratio by ¹H NMR. ¹H NMR (C₆D₆): δ 4.05 (SiH).

Et₂SiH-Capped Syndiotactic Polystyrene. On the vacuum line, toluene (50 mL) was condensed into a flamed, 100 mL reaction flask equipped with a magnetic stirring bar and a septum-covered sidearm. Next, 3.0 mL (23.12 mmol) of Et₂SiH₂ and 1.0 mL of styrene were vacuum transferred into the flask at -78°C . In the glovebox, a 6 mL sample vial equipped with a septum cap was loaded with 12 mg (0.053

mmol) of (Me₅C₅)TiMe₃ and 30 mg (0.033 mmol) of Ph₃C⁺B(C₆F₅)₄⁻. A measured amount of toluene (2.0 mL) was then syringed into the vial with a dry, Ar-purged gastight syringe. The vial was removed from the glovebox immediately prior to the polymerization experiment, and the catalyst solution was quickly syringed under an Ar counterflow into the rapidly stirred olefin + silane reaction mixture at 55°C through the septum-sealed reaction flask sidearm. After 3 min, the reaction was quenched by addition of 2.0 mL of methanol. The polymeric product was collected by filtration and then washed with methanol and acetone, followed by drying under vacuum. Yield, 0.68 g. $M_n = 43\,000$ by ¹H NMR. ¹H NMR (relative intensity, C₂D₂Cl₄, 120°C): δ 7.07 (100, Ph), 6.56 (66, Ph), 3.42 (0.07, SiH), 1.82 (31, –CH–), 1.28 (64, –CH₂–), 0.90 (0.24, –CH₃), 0.78 (0.22, CH₂Si). ¹³C NMR (C₂D₂Cl₄, 75.5°C , 120°C): δ 145.1, 128.8, 127.7, 43.5, 40.4, 35.2, 20.0, 19.8, 1.2.

Et₂HSi-Capped Polypropylene. Method A. On the vacuum line, toluene (50 mL) was condensed into a flamed, 250 mL reaction flask equipped with a magnetic stirring bar and a septum-covered sidearm. Next, 3.5 mL (27.0 mmol) of Et₂SiH₂ was vacuum transferred into the flask at -78°C . The mixture was then warmed to 25°C and exposed to propylene (1 atm) while being stirred rapidly. In the glovebox, a 6 mL sample vial equipped with a septum cap was loaded with 14 mg (0.043 mmol) of [Me₂Si(Me₄C₅(^tBuN))]TiMe₂ and 30 mg (0.033 mmol) of Ph₃C⁺B(C₆F₅)₄⁻. A measured amount of toluene (2.0 mL) was then syringed into the vial with a dry, Ar-purged gastight syringe. The vial was removed from the glovebox immediately prior to the polymerization experiment, and the catalyst solution was quickly syringed under a propylene counterflow into the rapidly stirred olefin + silane reaction mixture at 25°C through the septum-sealed reaction flask sidearm. After 5 h, the reaction was quenched by addition of 2.0 mL of methanol, and the polymer was collected by filtration and then extracted with *n*-pentane (50 mL). The polymer was isolated by evaporating the solvent and washing the product with methanol and acetone, followed by drying under vacuum. Yield, 2.94 g; 60% of the polypropylene was determined to be silyl-terminated by ¹H NMR. ¹H NMR (C₆D₆): δ 4.20 (SiH).

Method B. On the vacuum line, toluene (50 mL) was condensed into a flamed, 100 mL reaction flask equipped with a large magnetic stirring bar and a septum-covered sidearm. Next, 3.0 mL (23.1 mmol) of Et₂SiH₂ was vacuum transferred into the flask at -78°C . The mixture was then warmed to room temperature and exposed to propylene (1 atm) while being stirred rapidly. In the glovebox, a 6 mL sample vial equipped with a septum cap was loaded with 12 mg (0.053 mmol) of (Me₅C₅)TiMe₃ and 30 mg (0.033 mmol) of Ph₃C⁺B(C₆F₅)₄⁻. A measured amount of toluene (2.0 mL) was then syringed into the vial with a dry, Ar-purged gastight syringe. The vial was removed from the glovebox immediately prior to the polymerization experiment, and the catalyst solution was quickly syringed under a propylene counterflow into the rapidly stirred olefin + silane reaction mixture at 25°C through the septum-sealed reaction flask sidearm. After 12 min, the reaction was quenched by addition of 2.0 mL of methanol. The product was collected by filtration and then extracted with *n*-pentane (50 mL). The polymer was isolated by filtration, the solvent evaporated from the filtrate, and the product washed with methanol and acetone, followed by drying under vacuum. Yield, 4.03 g. $M_n = 142\,400$, $M_w = 312\,700$ by GPC. End groups were not observed due to the high molecular weight. ¹H NMR (C₆D₆, 300 MHz): δ 1.76 (–CH–, 31), 1.19 (–CH₂–, 60), 0.97 (–CH₃, 100).

Synthesis of Polypropylene/Polystyrene AB Block Copolymer. On the vacuum line, 1.0 g of PhH₂Si-capped polypropylene ($M_n = 3300$) was placed in a flamed, 100 mL reaction flask equipped with a magnetic stirring bar and a septum-covered sidearm under an Ar counterflow. Then, 60 mL of toluene was condensed into the flask to dissolve the polymer. Next, 3.0 mL of styrene was vacuum transferred into the flask at -78°C . In the glovebox, a 6 mL sample vial equipped with a septum cap was loaded with 15 mg (0.066 mmol) of (Me₅C₅)TiMe₃ and 40 mg (0.043 mmol) of Ph₃C⁺B(C₆F₅)₄⁻. A measured amount of toluene (2.0 mL) was then syringed into the vial with a dry, Ar-purged gastight syringe. The vial was removed from the glovebox immediately prior to the polymerization experiment, and the catalyst solution was syringed under an Ar counterflow into the rapidly stirred

Table 1. Comparison of Cocatalyst Effects in the Polymerization of Propylene in the Presence of PhSiH₃

entry	catalyst ^a	cocatalyst ^b	time (h)/temp (°C)	polymer yield (g)	activity (kg of PP/mol of Ti atm h)
1	[Me ₂ Si(Me ₄ C ₅) ^t BuN]TiMe ₂	Ph ₃ C ⁺ B(C ₆ F ₅) ₄ ⁻	1/25	7.0	14
2	[Me ₂ Si(Me ₄ C ₅) ^t BuN]TiMe ₂	B(C ₆ F ₅) ₃	20/25	0.05	0.005

^a Concentration of catalyst is 0.50 mM. ^b 1.0 equiv of cocatalyst used.

reaction mixture through the septum-sealed reaction flask sidearm at 120 °C. After 12 h, the reaction was quenched by addition of 2.0 mL of methanol. The product was collected by filtration and then refluxed with *n*-heptane to remove any unreacted PhH₂Si-capped polypropylene (identity verified by ¹H NMR). About 0.88 g of the unreacted PhH₂-Si-capped polypropylene was recovered. The insoluble polymeric product was then collected by filtration and washed with methanol and acetone, followed by drying under vacuum. Yield, 1.59 g. *M*_n = 33 600, *M*_w = 204 700 by GPC. ¹H NMR (relative intensity, C₂D₂Cl₄): δ 7.40–6.80 (100, *Ph*), 6.35 (66, *Ph*), 1.85 (21, *-CH-*), 1.35 (40, *-CH₂-*), 0.90 (4.33, *-CH₃*). ¹³C NMR (C₂D₂Cl₄, 75.5 MHz): δ 145.2, 127.8, 127.6, 125.5, 43.6, 40.5, 35.3, 27.3, 20.4, 20.1, 19.8, 1.2. ²⁹Si NMR (C₂D₂Cl₄, 79.5 MHz): δ -3.42. *T*_m = 272 °C.

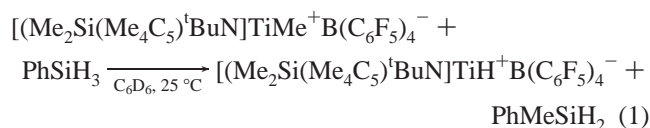
Attempted One-Pot Synthesis of an AB Block Copolymer. On the vacuum line, toluene (20 mL) was condensed into a flamed, 100 mL reaction flask equipped with a large magnetic stirring bar and a septum-covered sidearm. Next, 1.0 mL (6.0 mmol) of PhSiH₃ was vacuum transferred into the flask at -78 °C. The mixture was then warmed to 25 °C and exposed to propylene (1 atm) while being stirred rapidly. In the glovebox, a 6 mL sample vial equipped with a septum cap was loaded with 11 mg (0.031 mmol) of [Me₂Si(Me₄C₅)^t(BuN)]-TiMe₂ and 28 mg (0.030 mmol) of Ph₃C⁺B(C₆F₅)₄⁻. A measured amount of toluene (2.0 mL) was then quickly syringed into the vial with a dry, Ar-purged gastight syringe. The vial was removed from the glovebox immediately prior to the polymerization experiment, and the catalyst solution was syringed under a propylene counterflow into the rapidly stirred reaction mixture at 25 °C through the septum-sealed reaction flask sidearm. After 5 min, the flask was evacuated, and the reaction temperature was then raised to 110 °C. In the glovebox, another 6.0 mL sample vial equipped with a septum cap was loaded with 11 mg (0.048 mmol) of (Me₅C₅)TiMe₃ and 30 mg (0.033 mmol) of Ph₃C⁺B(C₆F₅)₄⁻. A measured amount of toluene (2.0 mL) was then syringed into the vial with a dry, Ar-purged gastight syringe. Next, 3.0 mL of styrene and the catalyst solution were sequentially injected by syringe under an Ar counterflow into the rapidly stirred 110 °C reaction mixture through the septum-sealed reaction flask sidearm. After being stirred for 16 h, the reaction was quenched by addition of 2.0 mL of methanol. The product was collected by filtration and then refluxed with *n*-heptane to remove any polypropylene. The residue was collected by filtration and then washed with methanol and acetone, followed by drying under vacuum. Yield, 2.50 g. The product is a mixture of highly syndiotactic (*rr* > 97%) PhH₂Si-capped polystyrene, polypropylene-(Ph)(H)Si-polystyrene block copolymer, and uncapped polystyrene, in a ratio of ~1:6:1.

Results and Discussion

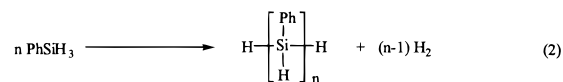
In this section, the synthesis and characterization of several families of silyl-capped stereoregular and -irregular polyolefin homo- and copolymers, produced with single-site organo-group 4 catalysts, are described. Next, the reactivities of primary and secondary silanes as chain-transfer agents are compared. These chain-transfer processes are then shown to provide catalytic routes to linear A-A and “star” block copolymers. Finally, polystyrene/polypropylene block copolymers are produced using silapolypropylene as the chain-transfer agent.

Organo-Group 4-Mediated Stoichiometric M-C/Si-H Transposition. In research preceding this study, we reported that silyl-capped polyethylenes and ethylene-based copolymers were efficiently produced via organolanthanide catalysts (Scheme 1).¹³ There are, however, significant deficiencies of this process: (i) limitation to ethylene-based polymerizations, (ii) low levels of comonomer incorporation, and (iii) limited large-

scale acceptance of the organolanthanide catalysts. To address these drawbacks, we focused on “single-site” group 4 catalyst systems^{1,10} which have broad applicability beyond ethylene-based polymerizations, are well-accepted, and are mechanistically understood in some depth for α-olefin polymerization.^{1,10} In one of a number of model test reactions for M-C/Si-H transposition, the reaction of [Me₂Si(Me₄C₅)^tBuN]TiMe⁺B(C₆F₅)₄⁻ with PhSiH₃ was investigated. As monitored by ¹H NMR, clean and rapid Ti-C/Si-H transposition occurs, yielding PhMeSiH₂ and what is presumably a cationic organotitanium hydride (eq 1).²⁴ These observations motivated detailed investigation of silane effects on single-site olefin polymerization systems.



A. Silyl-Capped Atactic Polypropylenes (Atactic Silapolypropylene). Propylene polymerizations were carried out in the presence of PhSiH₃ under rigorously anhydrous/anaerobic conditions and using methodology designed to minimize mass-transfer effects.²⁵ Interestingly, a variety of *zirconium* and *hafnium* metallocenes ((Me₅C₅)₂ZrMe₂, (1,2-Me₂C₅H₃)₂ZrMe₂, (Me₅C₅)₂HfMe₂) and quasi-metallocenes ([Me₂Si(Me₄C₅)^tBuN]-ZrMe₂) with a variety of cocatalysts produced predominantly or exclusively polyolefins devoid of silyl caps, together with dehydrogenative silane coupling (eq 2)²⁶ products (PhH₂Si-SiH₂Ph, etc.), as judged by ¹H NMR. The behavior of “cationic”



organotitanium catalysts is markedly different, however, with the efficacy in producing silyl-capped atactic polypropylene strongly sensitive to the cocatalyst. Thus, for the formation of atactic silapolypropylene using PhSiH₃ as the chain-transfer agent, [Me₂Si(Me₄C₅)^tBuN]TiMe⁺B(C₆F₅)₄⁻ is ~2800 times more active than [Me₂Si(Me₄C₅)^tBuN]TiMe⁺MeB(C₆F₅)₃⁻ under the same reaction conditions (Table 1). This ordering is similar to observations for [(Me₂Si(Me₄C₅)^tBuN]TiR⁺-mediated polymerizations in the absence of a silane,²⁴ and the results together argue that relative anion coordinative tendencies/ion-pairing tightness strongly modulate the activity of [(Me₂Si(Me₄C₅)^tBuN]TiR⁺X⁻ catalysts.^{24,27} These results also suggest that coordinatively more open catalysts may more readily

(24) Attempts to identify cationic organotitanium hydride complexes in the reaction of [Me₂Si(Me₄C₅)^tBuN]TiMe⁺B(C₆F₅)₄⁻ with PhSiH₃ were inconclusive. The reaction yields a mixture of unidentified oily species, presumably because the anion coordination is too weak to stabilize the highly electrophilic cation: Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842–857.

(25) Chen, Y.-X.; Metz, M. V.; Li, L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 6287–6305.

(26) Dioumaev, V. K.; Harrod, J. F. *J. Organomet. Chem.* **1996**, *521*, 133–143.

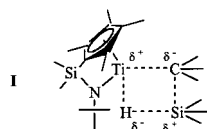
(27) (a) Xu, G. X.; Lin, S. A. *Acta Polym. Synth.* **1997**, *3*, 380. (b) Pellecchia, C.; Pappalardo, D.; D'Arco, M.; Zambelli, A. *Macromolecules* **1996**, *29*, 1158.

Table 2. $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{t-BuN})\text{TiMe}^+\text{B}(\text{C}_6\text{F}_5)_4^-]$ -Mediated Propylene and 1-Hexene Polymerization: Ethylene–1-Hexene, Ethylene–Styrene, and Propylene–1-Hexene Copolymerization in the Presence of PhSiH_3

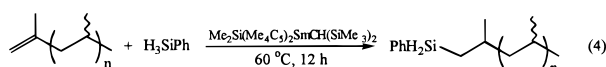
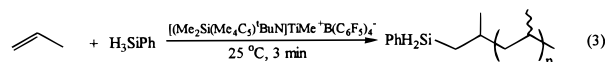
entry	time (min)/ temp (°C)	monomer (1 atm)	comonomer (M)	PhSiH_3 (M)	polymer yield (g)	comonomer incorp (M%)	activity (g/mol of Ti atm h)	M_n^b	M_w/M_n^b
1	3/25	propylene		0.03	3.0		1.91×10^6	43 000	3.5
2	3/25	propylene		0.05	2.5		1.64×10^6	24 200	1.7
3	3/25	propylene		0.08	1.3		1.06×10^6	20 300	2.0
4	3/25	propylene		0.40	0.4		6.55×10^5	7 500	2.1
5	3/25	propylene		0.73	3.8		2.49×10^6	1 100	4.4
6	3/25	propylene		1.13	3.2		2.10×10^6	890	5.0
7	10/0	propylene		0.020	4.0		7.86×10^5	67 000	3.1
8	60/25	1-hexene ^c		0.030	3.1		1.02×10^5	2 500	2.5
9	180/2	ethylene	0.17 ^d	0.050	2.8	50	3.06×10^4	72 000	1.4
10	180/2	ethylene	0.32 ^e	0.060	2.6	52	2.84×10^4	50 000	2.4
11	3/25	propylene	1.60 ^e	0.228	25.0	18	1.64×10^6	10 600	3.5

^a Concentration range of catalyst = 2.64–3.05 mM. ^b By GPC in 1,2,4-trichlorobenzene vs. polystyrene standards. ^c Concentration of 1-hexene = 6.00 M. ^d Styrene. ^e 1-Hexene.

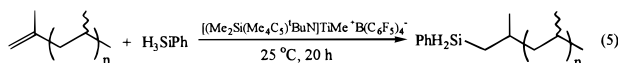
accommodate incoming chain-transfer agents and facilitate the formation of what are presumably four-centered σ -bond metathesis transition states (e.g., **I**).



The “constrained geometry” $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)\text{t-BuN}]\text{TiMe}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ catalyst mediates rapid polymerization of propylene with efficient silanolytic chain transfer (Table 2), with no detectable silane dehydro coupling products^{18,26,28} (by ^1H , ^{29}Si NMR). The PhH_2Si -capped atactic polypropylenes (eq 3) were characterized by $^1\text{H}/^{13}\text{C}$ NMR, GPC, IR, and comparison with an authentic sample prepared via conventional organolanthanide-catalyzed hydrosilylation (eq 4).¹⁵ An alternative group 4-medi-



ated route to silapolypropylenes could conceivably be via hydrosilylation of an exogenous vinylidene-terminated polypropylene formed by β -hydrogen elimination or some other chain-transfer process.¹ However, control experiments argue that $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)\text{t-BuN}]\text{TiMe}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -catalyzed hydrosilylation does not contribute significantly to eq 3, since far longer reaction times are required for complete hydrosilylation under conditions identical to those for polymerization (eq 5). NMR spectra of



the PhH_2Si -capped atactic polypropylenes are in accord with the proposed microstructure. Thus, the ^1H NMR (Figure 1A) exhibits a characteristic PhSiH_2 resonance²⁹ (δ 4.48 ppm) coupled to an adjacent CH_2 (triplet, $^3J = 3.6$ Hz; resolved in lower M_w samples; SiH_2 diastereotopism not resolved) and a SiCH_2 resonance at δ 0.75 ppm (triplet, $^3J = 3.6$ Hz). In the ^{13}C NMR,

(28) (a) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22–29. (b) Corey, J. Y.; Huhmann, J. L.; Zhu, X.-H. *Organometallics* **1993**, *12*, 1121–1130. (c) Kobayashi, T.; Sakakura, T.; Hayashi, T.; Yumura, M.; Tanaka, M. *Chem. Lett.* **1992**, 1157–1160.

(29) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1984; pp 512–520.

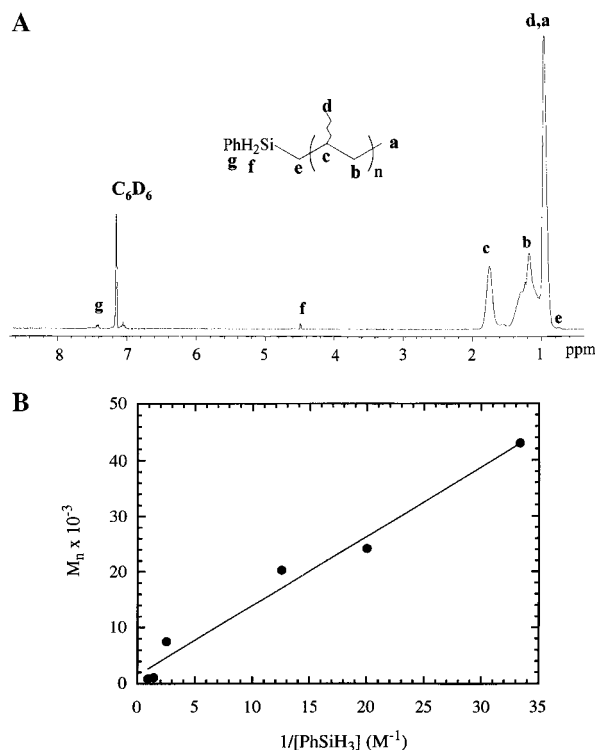


Figure 1. (A) ^1H NMR spectrum (300 MHz) of a PhH_2Si -capped atactic polypropylene sample in C_6D_6 at 25°C . (B) Relationship of polypropylene number-average molecular weight (GPC versus polystyrene) to PhSiH_3 chain-transfer agent concentration in the $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)\text{t-BuN}]\text{TiMe}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -mediated capping of atactic polypropylene. Catalyst and olefin concentrations are held constant (Table 3, entries 1–6).

both SiCH_2 (δ 1.95 ppm; $^1J_{\text{C-H}} = 118$ Hz, triplet) and chain-end CH_3 (δ 14.53 ppm, $^1J_{\text{C-H}} = 124$ Hz, quartet) groups are readily assigned and present in essentially equal proportions. The ^1H NMR provides no evidence for unsaturated end groups indicative of competing chain-transfer processes, and the ^{29}Si NMR (single resonance at δ –21 ppm) is consistent with exclusive formation of a PhH_2Si -polymer product.

Phenomenologically, observed polydispersities are reasonable for a homogeneous, metallocene-mediated process¹ (Table 2), and average molecular weights of the PhH_2Si -capped polypropylenes can be controlled by varying the PhSiH_3 concentration (Figure 1B), as in the organolanthanide-mediated ethylene homopolymerizations,¹³ with the lowest PhSiH_3 concentration yielding the highest molecular weight polymer. Catalytic activity is not significantly depressed by PhSiH_3 addition. Assuming

Table 3. $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)\text{BuN}]\text{TiMe}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -Mediated Propylene Polymerization in the Presence of PhMeSiH_2

entry	$[\text{PhMeSiH}_2]$ (M)	yield (g)	silapolypropylene content (%) ^b	M_n^c ($\times 10^{-3}$)	M_w/M_n^c
1	0.12	1.20	50		
2	0.26	2.80	75		
3	0.36	1.50	80		
4	0.55	2.70	100	3.3	4.38
5	0.87	2.10	100	3.0 ^d	

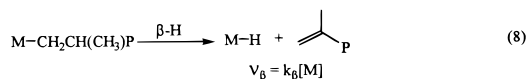
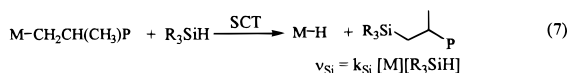
^a Concentration of catalyst = 1.55 mM. ^b Measured by ¹H NMR endgroup analysis. ^c Determined by GPC. ^d Determined by ¹H NMR.

constant catalyst, olefin, and silane concentrations, that rapid reinitiation occurs after chain transfer, and that silanolytic chain transfer is the dominant chain-transfer pathway under these conditions, \bar{P}_n at operational steady state should obey eq 6, where \bar{P}_n is the number average degree of polymerization, k_p the rate constant for chain propagation, and k_{Si} the rate constant for silanolytic chain transfer, and the other term(s) in the denominator accounts for all other uni- and bimolecular chain-transfer processes.³⁰ Experiments were carried out with constant

$$\bar{P}_n = \frac{k_p[\text{olefin}]}{k_{\text{Si}}[\text{H}_3\text{SiR}] + k_{\text{other chain-transfer processes}}[\text{Y}]^x} \quad (6)$$

catalyst and monomer concentration and $[\text{PhSiH}_3]$ varied but in all cases maintained in pseudo-zero-order excess. As can be seen in Figure 1B and Table 2, entries 1–6 obey this relationship, with $k_p/k_{\text{Si}} \approx 35$.³¹ For analogous $(\text{Me}_5\text{C}_5)_2\text{Sm}$ -mediated PhSiH_3 chain transfer in ethylene polymerization, $k_p/k_{\text{Si}} \approx 130$.¹³

To examine the scope of viable chain-transfer agents, secondary silanes were also examined in the same organotitanium-mediated propylene polymerization. As shown in Table 3, the efficacy of silanolytic chain transfer with more sterically encumbered PhMeSiH_2 is sensitive to reagent concentrations, with the highest yields of functionalized polymer derived from reactions carried out with relatively high PhMeSiH_2 concentrations. M–C/Si–H transposition is favored at high concentrations of chain-transfer agent (eq 7), with competing chain-transfer processes (e.g., β -hydrogen elimination, eq 8)^{1,32} competitive at low silane concentrations, and mixtures of silyl-capped and uncapped polypropylenes then produced. ¹H NMR end group



analysis is consistent with β -hydrogen elimination or chain transfer to monomer as the predominant competing chain-transfer pathway, indicated by vinylidene endgroups (δ 4.82

(30) (a) Tait, P. J. T.; Watkins, N. D. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, 1989; Vol. 4, pp 549–563. (b) Kissin, Y. V. *Isospecific Polymerization of Olefins*; Springer-Verlag: New York, 1985; Chapter I.

(31) For propylene solubility data in toluene, see: Wang, B. P. Ph.D. Dissertation, University of Massachusetts, 1989.

(32) (a) Kojoh, S.; Tsutsui, T.; Kashiwa, N.; Itoh, M.; Mizuno, A. *Polymer* **1998**, *39*, 6309–6313. (b) Murray, M. C.; Baird, M. C. *J. Mol. Catal.* **1998**, *128*, 1–4. (c) Kelly, W. M.; Wang, S. T.; Collins, S. *Macromolecules* **1997**, *30*, 3151–3158. (d) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015–10031. (e) Resconi, L.; Piemontesi, F.; Franciscano, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025–1032. (f) Eshuis, J. J.; Tan, Y. Y.; Teuben, J. H.; Renkema, J. J. *Mol. Catal.* **1990**, *62*, 277–287.

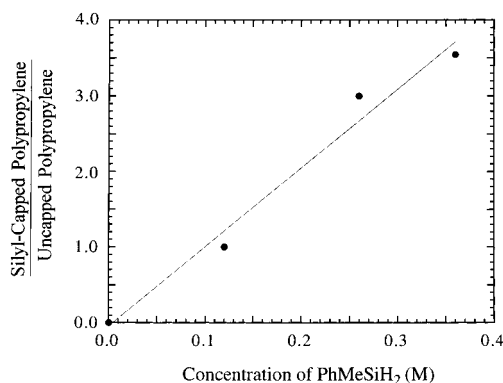
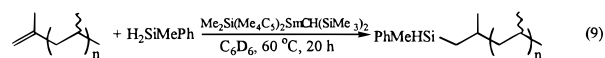


Figure 2. Ratio of silapolypropylene to polypropylene yield as a function of PhMeSiH_2 concentration in the $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)\text{BuN}]\text{-TiMe}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ -mediated propylene polymerization.

ppm, doublet).^{23,33} Hydrosilylation of an exogenous vinylidene-terminated polymeric product can be ruled out as a significant pathway in view of the sluggish kinetics demonstrated in eq 5. The assignment of PhMeHSi -capped atactic polypropylene was confirmed by preparation of an authentic sample via hydrosilylation of preformed vinylidene-terminated polypropylene²³ with PhMeSiH_2 (eq 9). The product exhibits a single MePhSiH



¹H resonance at δ 4.60 ppm and a ²⁹Si signal at δ –2.0 ppm as the only observable ²⁹Si peak. The latter is a field position characteristic of tertiary silanes.^{15,29}

The product mix dependence on silane concentration is approximately linear (Figure 2). Pragmatically assuming the simplest case of two competing chain-transfer processes (β -hydrogen elimination and silanolytic chain transfer) and constant [propylene], the β -hydrogen elimination rate should depend only on the concentration of active catalyst (eq 8),³⁴ while the silanolytic chain-transfer rate should be proportional to the active catalyst concentration and [silane] (eq 7). In this simple scenario, the capped polymer fraction should scale linearly with silane concentration (eq 10), as observed (Figure 2).

$$\frac{v_{\text{Si}}}{v_{\beta}} = \frac{k_{\text{Si}}[\text{M}][\text{R}_2\text{SiH}_2]}{k_{\beta}[\text{M}]} \quad (10)$$

It was previously noted that potentially coordinating silane chain-transfer agent aryl substituents are not kinetically significant in organolanthanide-mediated ethylene polymerization.¹³ However, the behavior of the organotitanium/propylene system is somewhat different, and change in chain-transfer agent from PhMeSiH_2 to Me_2SiH_2 and Et_2SiH_2 under identical conditions results in both a significant decrease in silyl-capped polypropylene yield (higher fraction of uncapped product) and an increased capped product molecular weight (Table 4, entry 1).

(33) (a) Guo, Z.; Swenson, D.; Jordan, R. F. *Organometallics* **1994**, *13*, 1424–1432. (b) Hajela, S.; Bercaw, J. E. *Organometallics* **1994**, *13*, 1147–1154. (c) Alelyunas, Y. W.; Guo, Z.; LaPointe, R. E.; Jordan, R. F. *Organometallics* **1993**, *12*, 544–553.

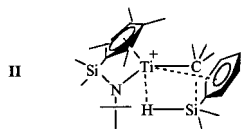
(34) (a) Since [propylene] is held constant, the rate of any chain transfer to monomer should also be invariant, and in any case, it is not obvious why a vinylidene-producing elimination pathway would be enhanced with increasing [silane]. (b) Cavallo, L.; Guerra, G.; Corradini, P. *J. Am. Chem. Soc.* **1998**, *120*, 2428–2436. (c) Stehling, U.; Diebold, J.; Kirsten, R.; Röhl, W.; Brintzinger, H.-H.; Jüngling, S.; Müllhaupt, R.; Langhauser, F. *Organometallics* **1994**, *13*, 964–970. (d) Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Polymer* **1989**, *30*, 429–431.

Table 4. Propylene Polymerization in the Presence of Secondary Silanes as Chain-Transfer Agents

entry	R ₂ SiH ₂ /[R ₂ SiH ₂] (M)	catalyst ^a	silapolypropylene yield (g)	time (min)	M _n ^b (× 10 ⁻³)	M _w /M _n ^b
1	Me ₂ SiH ₂ /0.10	[CGCTiMe] ⁺ [B(C ₆ F ₅) ₄] ⁻	2.1 ^c	10	51.0	2.45
2	Me ₂ SiH ₂ /0.49	[(Me ₅ C ₅)TiMe ₂] ⁺ [B(C ₆ F ₅) ₄] ⁻	1.6	10	36.9	4.25
3	Et ₂ SiH ₂ /0.46	[(Me ₅ C ₅)TiMe ₂] ⁺ [B(C ₆ F ₅) ₄] ⁻	4.0	12	142.4	2.20
4	Et ₂ SiH ₂ /0.60	[(Me ₅ C ₅)TiMe ₂] ⁺ [B(C ₆ F ₅) ₄] ⁻	3.9	10	106.6	2.42

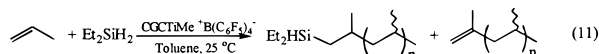
^a Concentration range of catalyst = 0.31–0.66 mM. ^b Determined by GPC. ^c Approximately 60% silapolypropylene.

This argues that aryl-substituted chain-transfer agents are more effective chain-transfer agents, the differences possibly reflecting a preordinating tendency of the silane aryl substituent (**II**), which may lower the barrier to Si–H/Ti–polyolefin transposition, thereby resulting in lower polymer molecular weights. Arene coordination has previously been observed in CGCZrMe⁺

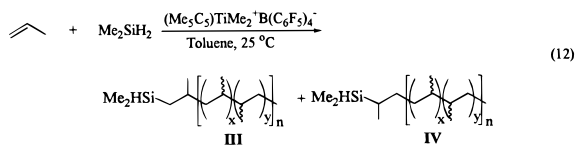


chemistry.²⁴ Alternatively, the capping efficiency effect may primarily reflect differences in Si–H bonding energetics, since *D*(Si–H) in Me₂SiH₂ is ~2 kcal/mol larger than that in PhSiH₃.^{12f,35} The higher molecular weight of the Et₂SiH-capped polypropylene vs that of Me₂SiH-capped polypropylene (Table 4, entries 3–5) using a more open catalyst (*vide infra*) is likely steric in origin (*k*_{Si} is smaller).

In the case of Et₂SiH₂ as the chain-transfer agent, a mixture of silyl-capped and uncapped polypropylene in a ratio of 3:2 (eq 11) is obtained in the presence of the CGCTi catalyst.



Throughout the series of secondary silane chain-transfer reactions, as noted above, there is a competition between silanolytic chain transfer and other chain-transfer processes (e.g., β-H elimination), which is presumably influenced by silane–catalyst steric repulsions. To further decrease these steric impediments, less sterically hindered monocyclopentadienyl titanium complexes and Me₂SiH₂ were investigated (Table 4). Me₂SiH₂ is potentially abundant as a byproduct of the “direct process”.³⁶ Propylene polymerization was carried out under conditions similar to those for PhSiH₃ + propylene above (Table 4). As shown in eq 12, the reaction of Me₂SiH₂ + propylene exclusively affords Me₂HSi-capped atactic polypropylene, however with mixed (1:1 ratio) 1,2 and 2,1 regiochemistry of propylene enchainment. This regiochemical result is identical

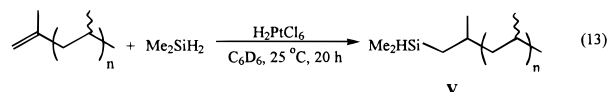


to Baird's observations on [(Me₅C₅)TiMe₂]⁺[B(C₆F₅)₄]⁻-mediated propylene polymerization, but in the absence of Me₂SiH₂.³⁷ The microstructure of the Me₂HSi-capped polypropylene

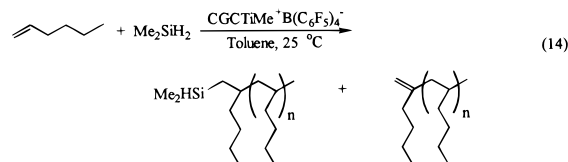
(35) Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; pp 371–391.

(36) For references on the direct process, see: (a) Sun, D. H.; Bent, B. E.; Wright, A. P.; Naasz, B. M. *Catal. Lett.* **1997**, *46*, 127–132. (b) Friedrich, H. B.; Sevenich, D. M.; Gaspargalvin, L. D.; Rethwisch, D. G. *Anal. Chim. Acta* **1989**, *222*, 221–234. (c) Banholzer, W. F.; Burrell, M. C. *J. Catal.* **1988**, *114*, 259–270. (d) Rochow, E. G. *J. Am. Chem. Soc.* **1945**, *67*, 963. (e) Rochow, E. G. US Patent 2,380,995, 1945.

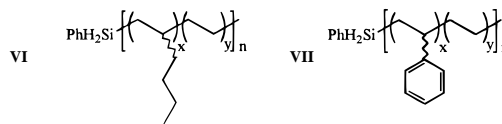
was confirmed by ¹H and ²⁹Si NMR. The ¹H NMR exhibits Me₂SiH resonances at δ 4.32 (**III**) and 3.98 ppm (**IV**) (Me₂SiH₂ = δ 3.82 ppm), while the ²⁹Si NMR shows signals at δ 5.4 (**III**) and 4.7 ppm (**IV**), respectively. Hydrosilylation of vinylidene-terminated polypropylene with Me₂SiH₂ in the presence of H₂PtCl₆ affords exclusively the 1,2-hydrosilylation product (**V**) with identical ¹H NMR and ²⁹Si NMR parameters (eq 13).



B. Silyl-Capped Atactic Poly(1-hexene) and Silyl-Capped Ethylene–α-Olefin Copolymers. Regarding monomer scope, the CGCTi catalyst mediates rapid 1-hexene homopolymerization in the presence of PhSiH₃, to yield silyl-capped poly(1-hexene). In contrast to the results with a primary silane, a mixture of silyl-capped poly(1-hexene) and uncapped poly(1-hexene) is obtained when Me₂SiH₂ is used as the chain-transfer agent (eq 14), again suggesting that chain-transfer efficiency is dominated by silane steric encumbrance during Ti–C/Si–H transposition.



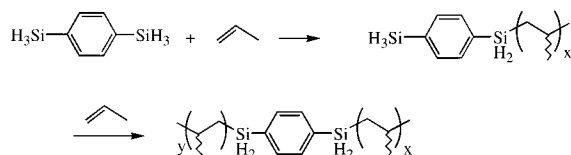
Interestingly, organotitanium-mediated chain transfer fails to yield primary and secondary silapolyethylene derivatives for ethylene homopolymerization at 25 °C (vinyl-terminated polyethylene is produced instead). That this result reflects complex competing kinetic and steric effects is suggested by the following observations: (i) organotitanium-mediated chain transfer to polyethylene is effective at –25 °C and (ii) organotitanium catalysts mediate efficient 25 °C chain transfer in ethylene + 1-hexene and ethylene + styrene copolymerizations, yielding products with high degrees of comonomer incorporation and in which, as indicated by NMR, Si is predominantly adjacent to 1,2-inserted comonomer units (**VI** and **VII**) (Table 2, entries 9, and 10). The degrees of comonomer incorporation in the



organotitanium-mediated silanolytic chain-transfer process are far higher than possible in the organolanthanide-mediated reactions¹³ (Table 2) and are typical of CGC catalysts.²⁰ The microstructures of **VI** and **VII** were assigned by ¹³C NMR. For **VI**, the ¹³C NMR exhibits PhSiH₂CH₂ spectral parameters (δ 14.4

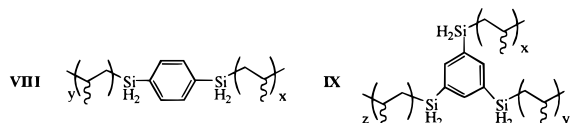
(37) Ewart, S. W.; Sarsfield, M. J.; Jeremic, D.; Tremblay, T. L.; Williams, E. F.; Baird, M. C. *Organometallics* **1998**, *17*, 1502–1510.

Scheme 3

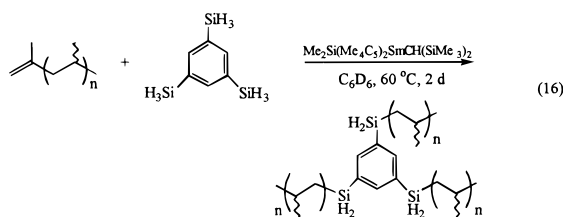
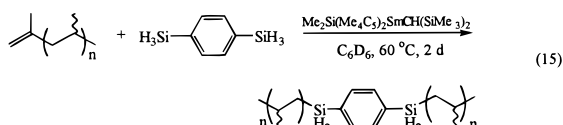


ppm, triplet, $^1J_{C-H} = 119$ Hz) identical to those in PhSiH₂-capped atactic poly(1-hexene). Furthermore, the PhSiH₂CH₂-CHPh ¹³C shift in **VII** is identical to that in PhSiH₂CH₂CH₂-Ph,^{15b} generated by organolanthanide-mediated hydrosilylation of styrene. The reason for preferential PhSiH₂ delivery to sites adjacent to comonomer enchainment is not immediately obvious on steric grounds but may reflect weaker Ti–C bonding.

C. AA and Starlike Block Copolymers. Most star and linear block copolymers are synthesized by living (anionic, cationic), or radical polymerization processes.³⁸ However, the present silanolytic chain-transfer process offers the possibility of synthesizing such structures catalytically. Propylene polymerization in the presence of polyfunctional chain-transfer agents such as 1,4-disilabenzene¹⁸ and 1,3,5-trisilabenzene¹⁸ produces macromolecular architectures **VIII** and **IX**, respectively. During

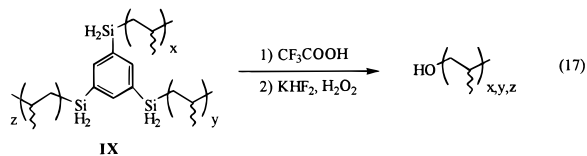


the course of the polymerization/chain-transfer reaction, the propylene concentration (pressure) was deliberately decreased to approximately parallel the conversion-dependent diminution in the SiH₃ groups to maximize the functionalization level and to minimize dispersion in *x*, *y*, *z*. The PhSiH₃ concentration at any time was estimated from $k_p/k_{si} = 35$ (eq 6) and previous estimates of k_p (~ 1390 M⁻¹ min⁻¹) for propylene and this catalyst under otherwise identical polymerization conditions (see Experimental Section for details).²⁵ ¹H NMR monitoring of these reactions reveals that polyfunctional reagents chain transfer occurs in an approximately stepwise fashion (e.g., Scheme 3), and this stepwise process, not unexpectedly, results in a broadened molecular weight distribution for **VIII** ($M_w/M_n = 4.3$). In the case of 1,3,5-trisilabenzene, the product exhibits a larger polydispersity ($M_w/M_n = 8.7$), as expected. Note that this system is, to our knowledge, the first in situ Ziegler catalytic synthesis of a starlike polymeric structure. ¹H NMR reveals SiH₂ chemical shifts of δ 4.52 (**VIII**) and 4.55 ppm (**IX**), observed as broad resonances. The ¹H NMR spectra are identical to those of the polymers produced via the corresponding hydrosilylation reactions (eqs 15 and 16). ²⁹Si NMR reveals the central Si



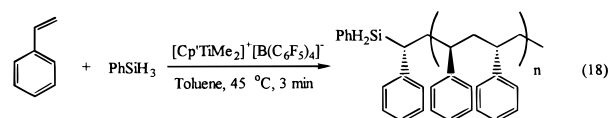
resonance in **VIII** at $\delta -34.0$ ppm and that in **IX** at $\delta -33.7$

ppm (the only observable signals). These data support the proposed secondary silane microstructures. C–Si scission in **IX** by protodesilylation and oxidative cleavage¹¹ produces HO-capped polypropylenes (eq 17), having a substantial polydispersity ($M_n = 3300$; $M_w/M_n = 7.6$). This result validates the



broadened chain length distribution assigned to **IX** and again supports the predominantly stepwise process shown in Scheme 3.

D. Silyl-Capped Stereoregular Polymers. The present chain transfer process can be applied to produce silyl-capped stereoregular polymers, as exemplified by syndiotactic polystyrene (eq 18). Polymerizations were carried out under a variety of



conditions in toluene using Cp^{*}TiMe₃ (Cp^{*} = η^5 -Me₅C₅) activated with Ph₃C⁺B(C₆F₅)₄⁻.³⁹ The optimized route to silyl-capped syndiotactic polystyrene employs styrene, Cp^{*}TiMe₃, and Ph₃C⁺B(C₆F₅)₄⁻ in the presence of PhSiH₃,⁴⁰ for 3 min at 45 °C. The crude product is then extracted with acetone to afford a 96% yield of insoluble product polymer. The product was characterized by ¹H and ¹³C NMR. In accord with a PhH₂Si-capped syndiotactic polystyrene microstructural assignment, the ¹H NMR exhibits diastereotopic PhSiH₂ resonances centered at δ 4.12 ppm coupled to an adjacent CH group (doublet of doublets with $^3J_{H-H} = 3.2$ Hz, $^2J_{H-H} = 6.4$ Hz; resolved in low-molecular-weight samples) and a –CHCH₃ (doublet with $^3J_{H-H} = 6.9$ Hz) endgroup (Figure 3A). As expected, the SiH₂:CH₃ intensity ratio is 2:3, indicating essentially equal proportions of the two end groups, as expected for Scheme 1. The phenyl ¹³C-1 resonance (δ 145.2 ppm) is a sharp singlet (Figure 3B) and can be assigned to the *rr* triad or *rrrr* pentad configuration,⁴¹ with syndiotacticity directly measured from the relative peak areas to be $\geq 98\%$. Furthermore, the presence of a silyl end group in this material is verified by a strong ν_{Si-H} absorption⁴² in the IR at 2155 cm⁻¹. Styrene polymerization and polymer charac-

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(40) The concentrations of silanes were maintained at a pseudo-zero-order level. Approximately 2 mol % of the PhSiH₃ was consumed during the polymerization.

(41) (a) Wang, Q.; Quyoum, R.; Gillis, D. J.; Tudoret, M.-J.; Jeremic, D.; Hunter, B. K.; Baird, M. C. *Organometallics* **1996**, *15*, 693–703. (b) Ready, T. E.; Day, R. O.; Chien, J. C. W.; Rausch, M. D. *Macromolecules* **1993**, *26*, 5822–5823. (c) Pellecchia, C.; Longo, P.; Proto, A.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 265–268. (d) Pellecchia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 277–279. (e) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2465–2466.

Table 5. (Me₃C₅)TiMe₂⁺B(C₆F₅)₄⁻-Mediated Styrene Polymerization in the Presence of PhSiH₃

entry	[CpTiMe ₃] (mM)	[PhSiH ₃] (M)	reactn temp (°C)	reactn time (min)	yield (g)	syndiotacticity ^a (%)	activity (kg of sPS/ mol of Ti atm h)	M _n ^b (× 10 ⁻³)	M _w /M _n ^b
1	0.040	0.86	40	6	0.96	97	313	20.4	1.39
2	0.060	0.41	45	3	4.48	98	1573	40.0	2.10
3	0.060	0.81	45	5	1.80	97	379	17.5	1.81
4	0.040	0.45	55	2	1.61	96	1102	13.1	3.73
5	0.040	0.20	55	2	0.56	98	383	60.5	1.16
6	0.040	0.41	60	3	1.78	97	812	13.0	1.38

^a Syndiotacticity assayed by ¹H NMR (400 MHz, C₂D₂Cl₄). ^b Determined by GPC versus polystyrene.

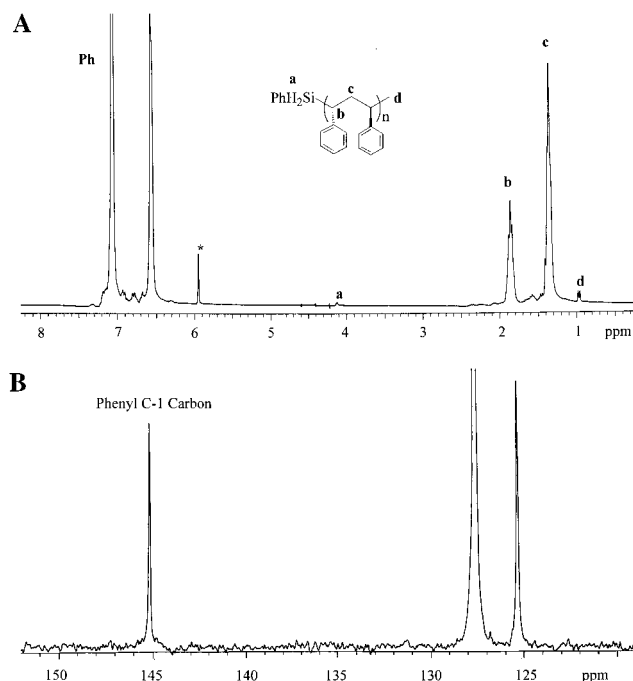


Figure 3. (A) ¹H NMR spectrum (300 MHz) of a PhH₂Si-capped syndiotactic polystyrene sample in C₂D₂Cl₄ at 120 °C. (B) ¹³C NMR spectrum (100 MHz) of a PhH₂Si-capped syndiotactic polystyrene sample in C₂D₂Cl₄ at 120 °C. The asterisk denotes solvent resonance (Cl₂HCCDCl₂).

terization data are summarized in Table 5. In entries 2–5, the silapolystyrene molecular weight is varied by the change in [PhSiH₃]. Not unexpectedly, the lowest PhSiH₃ concentrations correlate with the highest M_n polymers, although the reaction conditions are not always identical. The average molecular weight of the syndiotactic silapolystyrene products also decreases with increasing polymerization temperature (Table 5, entries 2 and 6), consistent with Campbell's observations made using a similar catalyst.⁴³ The high syndiotacticity and molecular weights of the capped polymers indicates that PhSiH₃ does not adversely affect the styrene enchainment stereochemistry³⁹ and depresses polymerization activity only slightly.

In addition to syndiotactic silapolystyrene, isotactic silapolypropylene can be produced from propylene in the presence of PhSiH₃ and [rac-C₂H₄(Ind)₂TiMe]⁺B(C₆F₅)₄⁻ at -45 °C (eq 19), albeit in low yield (characteristic of this catalyst).^{22,44} Isotacticity assayed by ¹³C NMR is found to be high (*mmmm*)

(42) (a) Pawlenko, S. *Organosilicon Chemistry*; Walter de Gruyter: New York, 1986; pp 137–138. (b) Crompton, J. R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1984; pp 416–421.

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(44) More efficient catalysts have recently been reported: Ewen, J. A.; Zambelli, A.; Longo, P.; Sullivan, J. M. *Macromol. Rapid Commun.* **1998**, *19*, 71–73.

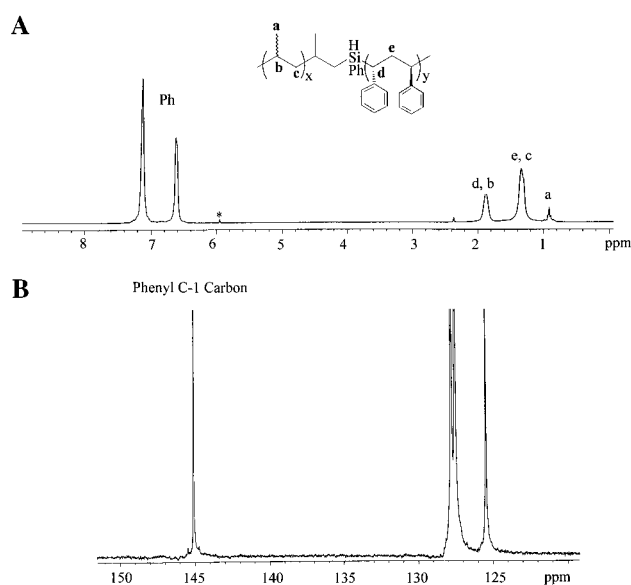
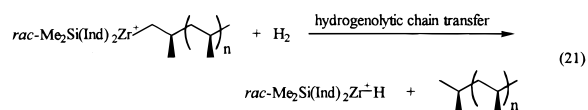
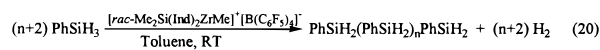
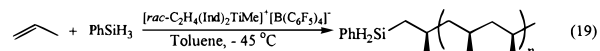
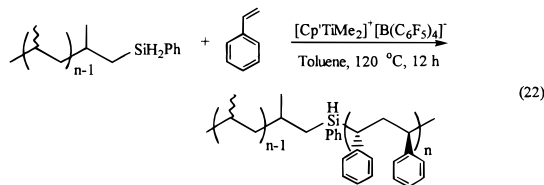


Figure 4. (A) ¹H NMR spectrum (300 MHz) of a polypropylene/polystyrene block copolymer sample in C₂D₂Cl₄ at 120 °C. (B) ¹³C NMR spectrum (75 MHz) of a polypropylene/polystyrene block copolymer sample in C₂D₂Cl₄ at 120 °C. The asterisk denotes solvent resonance (Cl₂HCCDCl₂).

= 94%). Other chiral Zr-based polymerization catalysts such as [rac-Me₂Si(Ind)₂ZrMe]⁺B(C₆F₅)₄⁻ afford uncapped isotactic polypropylene with saturated end groups. This suggests that dehydrogenative silane coupling predominates (eq 20), followed by hydrogenolytic chain transfer (eq 21).⁴⁵



E. Polypropylene/Polystyrene Block Copolymers. The present chain-transfer process can be extended to the synthesis of AB block copolymers by employing a silane-functionalized homopolymer as the chain-transfer agent. Thus, [Cp⁺TiMe₂]⁺[B(C₆F₅)₄]⁻ + styrene polymerization in the presence of atactic silapolypropylene (M_w = 3300; prepared via the approach of eq 3) yields atactic polypropylene (soft)–syndiotactic polystyrene (hard) block copolymers as the only product (eq 22) in ~60% yield (based on styrene monomer consumption). Note that this block copolymer is effectively and selectively produced in a *catalytic cycle* without graft or living polymerization.⁴⁶ The high reaction temperature prevents the polymerization solution from becoming overly viscous. After quenching of the reaction with MeOH, the isolated polymeric materials were refluxed in



n-heptane to remove unreacted silapolypropylene and small quantities of atactic polystyrene. The ^1H NMR spectrum of the copolymer product exhibits characteristic polypropylene CH_3 backbone (δ 0.89 ppm) and polystyrene CH and CH_2 backbone (δ 1.87, 1.26 ppm, respectively) resonances, which support the assignment of this product to a polypropylene–polystyrene block copolymer (Figure 4A). The Si–H resonance is too broad to be observed in the ^1H NMR spectrum due to the high molecular weight and spin–spin coupling ($M_n = 33\,600$, $M_w = 204\,700$). However, the ^{29}Si NMR exhibits a single feature at $\delta -3.42$ ppm which is close to that observed in PhMeHSi -capped atactic polypropylene ($\delta -2.00$ ppm). Despite the high reaction temperature, the tacticity of the polystyrene block is rather high (>97%, based on the phenyl C-1 ^{13}C NMR, Figure 4B) and exhibits high crystallinity ($T_m = 272$ °C).

Attempts to synthesize a similar block copolymer via a sequential one-pot procedure (PhSiH_3 + propylene + $\text{CGCTiMe}^+\text{B}(\text{C}_6\text{F}_5)_4^-$, then styrene + $\text{Cp}^*\text{TiMe}_2+\text{B}(\text{C}_6\text{F}_5)_4^-$) yielded a mixture of highly syndiotactic (>97%) PhH_2Si -capped polystyrene, the desired block copolymer, and small quantities of uncapped polystyrene, all of which could be identified by ^1H NMR endgroup analysis. The generation of PhH_2Si -capped polystyrene suggests plausible kinetic competition between PhSiH_3 and PhH_2Si -capped atactic polypropylene as chain-transfer agents. That is, unreacted PhSiH_3 from the propylene polymerization step acts as an efficient, competing chain-transfer agent in the polymerization of styrene.

(45) Alternatively, the regiochemistry of $\text{Zr}^+-\text{R}/\text{Si}-\text{H}$ transposition may be reversed from that in **I**, yielding Zr^+-Si and $\text{H}-\text{R}$. Zr^+-Si would then react²⁶ with $\text{Si}-\text{H}$ to yield Zr^+-H + $\text{Si}-\text{Si}$.^{25,27}

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Conclusions

The organotitanium-mediated silanolytic chain-transfer processes described herein afford a diverse variety of silyl-capped polyolefins with high selectivity and productivity. Cationic organotitanium catalysts and PhSiH_3 yield silyl-capped polyethylene at low temperatures, with vinyl-terminated polyethylene being the predominant product at higher temperatures. Nevertheless, silanolytic chain transfer is efficient in producing silyl-capped ethylene-based copolymers (ethylene + 1-hexene, ethylene + styrene) with relatively high comonomer incorporation. As the bulk of the monomer is increased to propylene and 1-hexene, silanolytic chain transfer becomes the dominant chain termination channel at room temperature. In the case of propylene polymerization, the molecular weight of the silapolypropylene product is efficiently controlled by the concentration of silane chain-transfer agent with negligible diminution in polymerization activity. In regard to the stereoregular macromolecules accessible, the syndiotacticity of silapolystyrene obtained is >98% and the isotacticity of silapolypropylene ~94%. These stereoregularities are comparable to those^{22,39} for polymerizations carried out in the absence of silane. The present chain-transfer process also facilitates construction of new silyl-linked polymer architectures. Thus, silyl-linked linear A–A and star block copolymers as well as AB block copolymers are produced in catalytic cycles using polyfunctional chain-transfer agents. The efficacy of silanolytic chain-transfer reactions with secondary silanes is sensitive to the silane substituents and catalyst ancillary ligation, with aryl substituents and single Me_5C_5 rings, respectively, being particularly effective. We have therefore demonstrated that primary and secondary silanes can effectively serve as chain-transfer agents in early transition metal-mediated olefin polymerization systems both to control molecular weight and to selectively produce silyl-capped and/or silyl-linked polyolefins.

Acknowledgment. This research was supported by the NSF (Grant CHE 9618589). K.K. thanks Dow Corning Corp. for a postdoctoral fellowship. We thank Dr. Peng-Fei Fu of Dow Corning Corp. for GPC analyses and Austin Chemical Co. (IL) and Asahi Glass Co., Ltd., for a generous donation of $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$.

Note Added in Proof. An analogous chain-transfer process has recently been reported for zirconocene catalysts and a borane: Xu, G.; Chung, T. C. *J. Am. Chem. Soc.* **1999**, *121*, 6763–6764.

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