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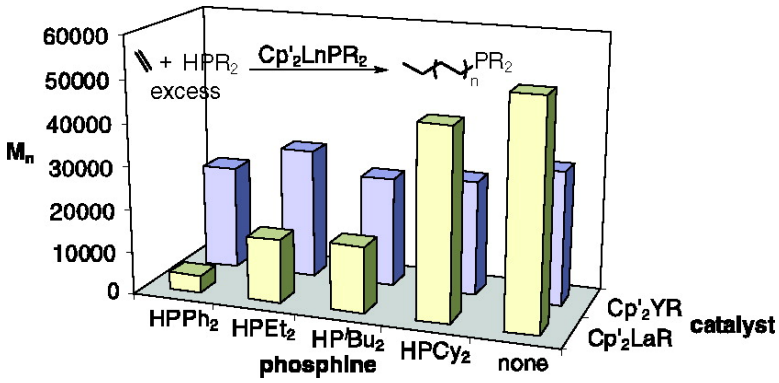
J. Am. Chem. Soc., **2005**, 127 (17), 6311-6324• DOI: 10.1021/ja044174i • Publication Date (Web): 08 April 2005



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Organolanthanide-Catalyzed Synthesis of Phosphine-Terminated Polyethylenes. Scope and Mechanism

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Abstract: Primary and secondary phosphines are investigated as chain-transfer agents for organolanthanide-mediated olefin polymerization. Ethylene polymerizations were carried out with $[Cp'_2LnH]_2$ and $Cp'_2LnCH(SiMe_3)_2$ ($Cp' = \eta^5$-Me_5C_5; Ln = La, Sm, Y, Lu) precatalysts in the presence of dicyclohexyl-, diisobutyl-, diethyl-, diphenyl-, cyclohexyl-, and phenylphosphine. In the presence of secondary phosphines, high polymerization activities (up to 10^7 g of polymer/(mol of Ln·atm ethylene·h)) and narrow product polymer polydispersities are observed. For lanthanocene-mediated ethylene polymerizations, the phosphine chain-transfer efficiency correlates with the rate of $Ln-CH(SiMe_3)_2$ protonolysis by the same phosphines and follows the trend $H_2PPh \gg H_2PCy > HPPh_2 > HPEt_2 \approx HP^iBu_2 > HPCy_2$. Under the conditions investigated, dicyclohexylphosphine is not an efficient chain-transfer agent for Cp'_2LaPCy_2- and Cp'_2YPCy_2-mediated ethylene polymerizations. Diisobutylphosphine and diethylphosphine are efficient chain-transfer agents for Cp'_2La-mediated polymerizations; however, phosphine chain transfer does not appear to be competitive with other chain-transfer pathways in Cp'_2Y-mediated polymerizations involving diisobutylphosphine. Regardless of the lanthanide metal, diphenylphosphine is an efficient chain-transfer agent for ethylene polymerization. Polymerizations conducted in the presence of primary phosphines produce only low-molecular-weight products. Thus, Cp'_2Y-mediated ethylene polymerizations conducted in the presence of phenylphosphine and cyclohexylphosphine produce low-molecular-weight phenylphosphine- and cyclohexylphosphine-capped oligomers, respectively. For Cp'_2YPPh_2-mediated ethylene polymerizations, a linear relationship is observed between M_n and [diphenylphosphine]$^{-1}$, consistent with a phosphine protonolytic chain-transfer mechanism.

Introduction

Organolanthanide complexes[1] are among the most active known catalysts for single-site Ziegler−Natta-type α-olefin polymerization.[2] Thus, $[Cp'_2LnH]_2$[3] ($Cp' = \eta^5$-Me_5C_5) and $[Me_2SiCp''_2LnH]_2$[4] complexes ($Cp'' = \eta^5$-Me_4C_5) polymerize ethylene with turnover frequencies exceeding 1800 s^{-1} at 1.0 atm ethylene pressure and yield polyethylenes with high molecular weights and narrow polydispersities. In addition, organolanthanide complexes effect the homopolymerization of polar monomers[5] as well as mediate the sequential block copolymerization of nonpolar and polar monomers.[6] For example, Yasuda and co-workers used Cp'_2LnR (Ln = Sm, Yb, Lu; R = H, Me) complexes to block copolymerize ethylene with methyl methacrylate (MMA), ethyl methacrylate, δ-valerolactone, and

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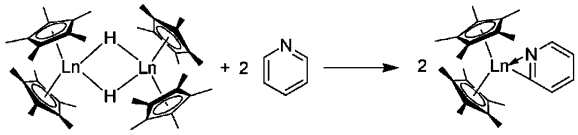
(5) Organolanthanide-mediated homopolymerization of polar monomers: (a) Sheng, E.; Zhou, S.; Wang, S.; Yang, G.; Wu, Y.; Feng, Y.; Mao, L.; Huang, Z. *Eur. J. Inorg. Chem.* **2004**, 2923. (b) Zhang, L.; Shen, Z.; Yu, C.; Fan, L. *Polym. Int.* **2004**, *53*, 1013. (c) Arndt, S.; Beckerle, K; Hültzsch, K. C.; Sinnema, P.-J.; Voth, P.; Spaniol, T. P.; Okuda, J. *J. Mol. Catal.* **2002**, *190*, 205. (d) Bala, M. D.; Hunag, J.; Zhang, H.; Qian, Y.; Sun, J.; Liang, C. *J. Organomet. Chem.* **2002**, *647*, 105. (e) Gromada, J.; Fouga, C.; Chenal, T.; Mortreux, A.; Carpentier, J.-F. *Macromol. Chem. Phys.* **2002**, *203*, 550. (f) Roesky, P. W.; Gamer, M. T.; Puchner, M.; Greiner, A. *Chem.−Eur. J.* **2002**, *8*, 5265. (g) Yasuda, H. *Prog. Polym. Sci.* **2000**, *25*, 573. (h) Li, Y.; Ward, D. G.; Reddy, S. S.; Collins, S. *Macromolecules* **1997**, *30*, 1875. (i) Li, F.; Jin, Y.; Song, C.; Lin, Y.; Pei, F.; Wang, F.; Hu, N. *Appl. Organomet. Chem.* **1996**, *10*, 761. (j) Giardello, M. A.; Yamamoto, Y.; Brard, L.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 3276. (k) Collins, S.; Ward, D. G.; Suddaby, K. H. *Macromolecules* **1994**, *27*, 7222. (l) Yasuda, H.; Tamai, H. *Prog. Polym. Sci.* **1993**, *18*, 1097. (m) Collins, S.; Ward, D. G. *J. Am. Chem. Soc.* **1992**, *114*, 5460. (n) Yasuda, H.; Yamamoto, H; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908. (o) Farnham, W. B.; Hertler, W. R. (E. I. du Pont de Nemours and Co.). U.S. Patent 901769 19860829, 1986.

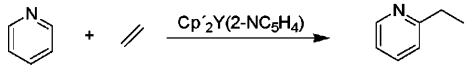
ϵ-caprolactone.[6h] The block copolymer of polyethylene and poly(MMA) represents a polymer with improved dyeability over nonfunctionalized polyethylene. The ability of organolanthanides to form polar and nonpolar monomer block copolymers thereby incorporates functionality into an otherwise inert polymer such as polyethylene and imparts improved physical polymer properties such as paintability, adhesion, and compatibility with other materials.

Another way of incorporating functionality[7−9] into polyolefins is by employing a chain-transfer agent.[10−14] However, there are few examples of efficient chain-transfer agents for organolanthanide-catalyzed olefin polymerization. Previously, our group reported that organosilanes act as efficient chain-transfer agents for organolanthanide-catalyzed olefin polymerizations as well as for ethylene and α-olefin copolymerizations.[13] Olefin polymerizations conducted in the presence of primary silanes ^{n}BuSiH$_3$, $C_6H_5SiH_3$, and $C_6H_5CH_2SiH_3$ produce silane-capped polymers with narrow molecular weight distributions. Unfortunately, secondary organosilanes do not act as efficient chain-transfer agents. Teuben and co-workers subsequently took advantage of the fact that lanthanocenes cleanly effect aryl C−H activation and synthesized Cp′$_2$Y(2-pyridyl) from [Cp′$_2$YH]$_2$ and pyridine (eq 1). In the presence of excess pyridine and ethylene, 2-ethylpyridine was produced catalytically using Cp′$_2$Y(2-pyridyl) (eq 2).[15] Unfortunately, only trace amounts of polymer were detected.



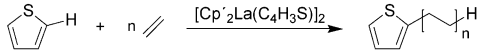
(1)

Cp′$_2$Y(2-pyridyl)



(2)

More recently, Hessen and co-workers investigated a similar transformation with thiophene and demonstrated the application of this heterocycle as a chain-transfer agent for organolanthanide-mediated ethylene polymerization (eq 3).[12] However, high ethylene pressures and high reaction temperatures are required to obtain modest polymerization activities and product molecular weights. With ethylene polymerizations conducted in the presence of thiophene or pyridine, the stability of the chelating monoinsertion products, Cp′$_2$LnCH$_2$CH$_2$(C$_4$H$_3$S) (Ln = Y, La) and Cp′$_2$YCH$_2$CH$_2$(2-C$_5$H$_4$N), is believed to inhibit facile chain propagation.



(3)

Cp′$_2$LnCH$_2$CH$_2$(C$_4$H$_3$S) (Ln = Y, La)

Cp′$_2$YCH$_2$CH$_2$(2-NC$_5$H$_4$)

As noted above, it had previously been shown that electron-deficient or electron−neutral reagents, such as boranes,[10] alanes,[11] and silanes,[13] can be used as chain-transfer agents for single-site f ^{n}/d^0-mediated olefin polymerizations; however, at the outset of the present study, the application of electron-rich reagents (e.g. groups 15, 16) as chain-transfer agents to afford polyolefins capped with electron-rich functional groups had not yet been efficiently realized. Organolanthanide complexes are efficient ethylene polymerization as well as hydroamination[16] and hydrophosphination[17,18] catalysts; therefore, an intriguing question arises as to whether the two types of transformations could be coupled to utilize phosphines or amines as chain-transfer agents for olefin polymerization. This would represent a new, efficient way of delivering an electron-rich and chemically versatile fragment to the terminus of a polyolefin chain.

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(11) Aluminum chain transfer: (a) Götz, C.; Rau, A.; Luft, G. *Macromol. Mater. Eng.* **2002**, *287*, 16. (b) Kukral, J.; Lehmus, P.; Klinga, M.; Leskelä, M.; Rieger, B. *Eur. J. Inorg. Chem.* **2002**, 1349. (c) Han, C. J.; Lee, M. S.; Byun, D. -J.; Kim, S. Y. *Macromolecules* **2002**, *35*, 8923. (d) Liu, J.; Støvneng, J. A.; Rytter, E. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3566. (e) Po', R.; Cardi, N.; Abis, L. *Polymer* **1998**, *39*, 959. (f) Kang, K. K.; Shiono, T.; Ikeda, T. *Macromolecules* **1997**, *30*, 0, 1231. (g) Mogstad, A. -L.; Waymouth, R. M. *Macromolecules* **1992**, *25*, 2282. (h) Resconi, L.; Piemontesi, F. Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025.

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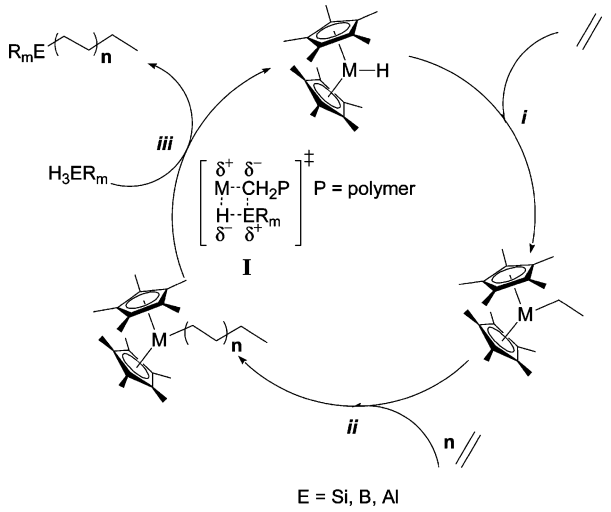
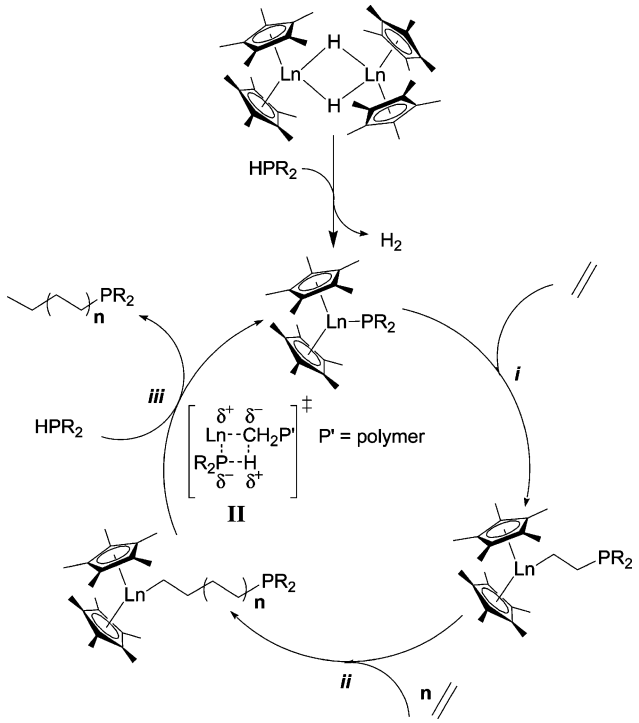
Scheme 1. Proposed Catalytic Cycle for Organolanthanide-Catalyzed Synthesis of Functional-Group Terminated Polyethylenes Using Electron-Deficient or Electron-neutral Chain-Transfer Agents



For electron-deficient or electron-neutral chain-transfer agents such as boranes[10] and silanes,[13] the heteroatom is chain-transferred to the polymer chain at the end of a hydride-based catalytic propagation sequence, with the chain-terminating C−heteroatom bond-forming step (Scheme 1, step iii) proposed to occur via four-centered σ-bond metathesis transition state **I**.

In contrast to organolanthanide-catalyzed formation of silyl-capped polyolefins, analogy drawn from hydrophosphination[17] and hydroamination[16,19] mechanistic observations argues that a cycle to incorporate electron-rich fragments would require C−heteroatom bond formation at the initiation of the chain-forming step (Scheme 2, step iii), with the Brønsted acidic E−H (E = P, N) subsequently effecting protonolytic chain transfer (transition state **II**). Therefore, a reasonable catalytic cycle for lanthanide-mediated synthesis of phosphine-capped polyethylenes (and, by implication, of amine-capped polyethylenes; Scheme 2) would require the following sequence of transformations: (i) insertion of C═C unsaturation into a lanthanide−phosphido bond, (ii) subsequent insertions of ethylene into the resulting Ln−C bond, and (iii) protonolytic cleavage of the propagating polyolefin chain by incoming phosphine substrate to close the cycle and regenerate the lanthanide−phosphido species.

Scheme 2. Proposed Catalytic Cycle for Organolanthanide-Catalyzed Synthesis of Phosphine-Terminated Polyethylenes



In a preliminary investigation, it was shown that organolanthanide-mediated ethylene polymerizations in the presence of a single phosphine chain-transfer agent, diphenylphosphine, yielded diphenylphosphine-capped polyethylenes, demonstrating that this is in fact a viable process, although neither the scope, kinetics, nor mechanism was defined.[20] In the present contribution, we extend the study to include a wider range of organolanthanide catalysts as well as a variety of secondary and primary phosphines in order to more fully investigate the scope of this organolanthanide-mediated synthesis of phosphine-capped polyethylenes. In addition, we present a full discussion of the scope, kinetics, and mechanism of such carbon−phosphorus bond-forming processes, focusing on the effect of phosphine substitution and lanthanide ion identity on the course and efficiency of the chain-transfer process.

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

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Schlenk line, or interfaced to a high-vacuum line (10^{-6} Torr), or in a nitrogen-filled Vacuum Atmospheres or MBraun glovebox with a high-capacity recirculator (<1 ppm of O_2). Argon and ethylene (Matheson, prepurified) were purified by passage through a MnO oxygen-removal column and a Davison 4-Å molecular sieve column. Hydrogen was purified by passage through a Q-5 oxygen-removal column heated to 75 °C and a Davison 4-Å molecular sieve column. Hydrocarbon solvents (pentane and toluene) were dried using an activated alumina column and Q-5 columns according to the method described by Grubbs,[21] and were additionally vacuum-transferred from Na/K alloy immediately before vacuum line manipulations. Benzene-d_6, toluene-d_8, chloroform-d, and 1,1,2,2-tetrachloroethane-d_2 were purchased from Cambridge Isotope Laboratories. Deuterated solvents used for NMR reactions were stored in vacuo over Na/K alloy in vacuum-tight storage flasks and were vacuum-transferred immediately prior to use. All organic starting materials were purchased from Aldrich Chemical Co. or Strem Chemicals, Inc. and were used without further purification unless otherwise stated. All of the phosphines were obtained commercially (Strem Chemicals, Inc.), distilled from CaH_2, distilled from Na/K, and stored in a vacuum-tight storage flask over activated Davison 4-Å molecular sieves. The organolanthanide precatalysts $Cp'_2LnCH(SiMe_3)_2$ ($Cp' = \eta^5$-Me_5C_5) and Cp'_2LnH (Ln = La, Sm, Y, Lu) were synthesized according to published procedures.[3]

Physical and Analytical Measurements. NMR spectra were recorded on either a Varian Gemini 300 (FT, 300 MHz, ^{1}H; 75 MHz, ^{13}C), Unity- or Mercury-400 (FT, 400 MHz, ^{1}H; 100 MHz, ^{13}C), or Inova-500 (FT, 500 MHz, ^{1}H; 125 MHz, ^{13}C) instrument. Chemical shifts (δ) for ^{1}H and ^{13}C are referenced to internal solvent resonances and reported relative to $SiMe_4$. Chemical shifts for ^{31}P are reported relative to an external 85% H_3PO_4 standard at room temperature. For polymer NMR characterization, 50−100 mg samples were dissolved in 0.5−0.7 mL of $C_2D_2Cl_4$ (Cambridge Laboratories) in a 5 mm NMR tube by heating the solution in a 125 °C oil bath.

MALDI-TOF MS spectra were collected on a PE Biosystems Voyager System 6050 time-of-flight mass spectrometer using a nitrogen laser for MALDI (λ = 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. GC−MS analyses were performed on a HP 6890 instrument equipped with a Zebron ZB-5 dimethylpolysiloxane column (30 m × 250 μm × 0.25 μm) attached to a HP 6890 mass-selective detector.

Polymer melting temperatures 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 (three columns, Waters Styragel HT 6E, HT 4, HT 2; operation temperature, 140 °C; mobile phase, 1,2,4-trichlorobenzene; flow rate, 1 mL/min) and reported relative to six polyethylene standards (M_w = 800, 1214, 2306, 13600, 32100, 119600) purchased from Polymer Laboratories Inc. Elemental analyses were performed by the Micro-Mass Facility at the University of California, Berkeley.

Synthesis of Bis(pentamethylcyclopentadienyl)(diphenylphosphido)-yttrium Cp'_2YPPh_2 (1). First, the hydride precatalyst $[Cp'_2YH]_2$ was generated in situ by stirring 250 mg (482 μmol) of $Cp'_2YCH(SiMe_3)_2$ in ~2 mL of toluene under 1.0 atm of H_2 for 2 h. Under an Ar flush, 85 μL (488 μmol) of diphenylphosphine was added via syringe. The resulting orange-red solution was stirred for 2 h at room temperature, and then all volatiles were removed in vacuo. Pentane was next condensed onto the residue, briefly stirred, and then all the volatiles were again removed in vacuo. Finally, ~3 mL of pentane was added, and the solution was cooled to −30 °C. Red-orange crystals were collected by decantation to obtain 160 mg (305 μmol) of **1** (63% yield). ^{1}H NMR (500 MHz, C_6D_6): δ 7.48 (t, J = 7.0 Hz, 4H), 7.05 (t, J = 7.0 Hz, 4H), 6.90 (t, J = 7.0 Hz, 2H), 1.85 (s, 30H). ^{13}C NMR (126 MHz, C_6D_6): δ 130.8 (d, J = 4.9 Hz), 127.0, 126.8, 124.2, 11.4 (d, J = 4.3 Hz); ^{31}P NMR (162 MHz, C_6D_6): δ −15.2 (d, J = 79 Hz). Anal. Calcd: C, 70.58; H, 7.40. Found: C, 70.68; H, 7.63.

Synthesis of 1-Eicosyldiphenylphosphine Oxide (2).[22] In a 100 mL Schlenk flask, 12 mL of 0.5 M $KPPh_2$ in THF (6.0 mmol) was added dropwise to 2.1 g (5.8 mmol) of 1-bromoeicosane in 40 mL of dry THF. The orange-red $KPPh_2$ solution turned colorless upon addition to the 1-bromoeicosane solution. The reaction mixture was stirred at room temperature overnight. Next, the solvent was removed in vacuo and 70 mL of pentane was added. Excess $KPPh_2$ was neutralized with deoxygenated H_2O. The colorless upper layer was then cannula-transferred away from the aqueous layer and dried over $MgSO_4$. The clear, colorless solution was cannula-filtered away from the $MgSO_4$, and the pentane was removed in vacuo. The resulting white powder was washed with 60 mL of deoxygenated MeOH and dried on a high-vacuum line at room temperature overnight. Next, a portion of the 1-eicosyldiphenylphosphine product (130 mg) was suspended in MeOH (5 mL), 30% H_2O_2 (0.2 mL) was added, and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was then extracted with pentane and dried over $MgSO_4$. The colorless solution was filtered and solvent was removed in vacuo to yield a white powder (110 mg). ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ 7.72 (t, 4H), 7.52−7.46 (m, 6H), 2.21 (m, 2H), 1.56 (m, 2H), 1.36 (m, 2H), 1.35−1.05 (br s, 32H), 0.87 (t, 3H). ^{13}C NMR (126 MHz, $C_2D_2Cl_4$): δ 135.3, 134.3, 133.2 (d, J = 1.8 Hz), 132.3 (d, J = 9.2 Hz), 130.2 (d, J = 11.9 Hz), 33.6, 32.6 (d, J = 14.7 Hz), 31.7, 31.4, 31.3, 31.1, 31.0, 30.8, 24.4, 23.1 (d, J = 3.7 Hz), 15.9. ^{31}P NMR (162 MHz, $C_2D_2Cl_4$): δ 32.1.

Catalytic Diphenylphosphine Oxide-Capped Polyethylene Synthesis Mediated by Isolated Cp'_2YPPh_2. Representative Experiment. In the glovebox, a three-necked Morton flask, which had been dried overnight on a high-vacuum line (10^{-6} Torr), equipped with a large stir bar and thermocouple (Omega type K stainless steel sheathed thermocouple), was charged with dry toluene (50 mL). The flask was then attached to a high-vacuum line, and ethylene (1.0 atm) was introduced. Diphenylphosphine (0.80 mL) was added via syringe to the reaction flask. In the glovebox, a solution of Cp'_2YPPh_2 (1.0 mg) in 1 mL of dry toluene was taken up in a 5-mL gastight syringe. The catalyst solution was then injected into the reactor with rapid stirring. A temperature rise was observed during the polymerization; therefore, the reaction was cooled by adding either ice or dry ice to a water bath. After 30 s, methanol (5 mL) was injected to quench the reaction. Excess methanol (~400 mL) was used to precipitate the polymer. The polymer (0.41 g) was then collected by filtration, washed with methanol (100 mL) and chloroform (100 mL), and dried in vacuo overnight. Next, 30% H_2O_2 (0.25 mL) was added to the diphenylphosphine-capped polyethylene (100 mg) suspended in 1.0 mL each of H_2O and methanol. The suspension was stirred for 4 h at room temperature, and the product was collected by filtration, washed with methanol and acetone, and dried in vacuo overnight.

Polymerization of Ethylene in the Presence of Diphenylphosphine. Representative Experiment. In the glovebox, a Teflon-valved storage tube, which had been dried overnight on the high-vacuum line (10^{-6} Torr) and equipped with a stir bar, was charged with $Cp'_2YCH(SiMe_3)_2$ (2.1 mg, 4.0 μmol) and dry toluene (1.16 mL). The storage flask was then attached to the vacuum line, and hydrogen (1.0 atm) was introduced. The precatalyst was stirred under hydrogen (1.0 atm) for 2 h at 20 °C and then stirred for an additional 2 h as a closed system. Next, diphenylphosphine (0.84 mL, 4.8 mmol) was added under an argon flush and the mixture stirred at 20 °C for 2 h. Next, the orange catalyst solution was cooled to −78 °C, and high vacuum was applied to remove trace amounts of hydrogen. In the glovebox, a three-necked Morton flask, which had been dried overnight on a high-vacuum line, 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,

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and ethylene (1.0 atm) was introduced with rapid stirring. The catalyst and phosphine solution were then injected into the reactor with rapid stirring. A temperature rise was observed during the polymerization; therefore, the reaction was cooled by adding either ice or dry ice to a surrounding water bath. After 30 s, methanol (5 mL) was injected to quench the reaction. Excess methanol (~400 mL) was then used to precipitate the polymer. The polymer (0.70 g) was collected by filtration, washed with methanol (100 mL) and chloroform (100 mL), and dried in vacuo overnight. Then 30% H_2O_2 (0.25 mL) was added to the diphenylphosphine-capped polyethylene (100 mg) suspended in 1.0 mL each of H_2O and methanol. The suspension was stirred for 4 h at room temperature, and the product was collected by filtration, washed with methanol and acetone, and dried in vacuo overnight. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ 7.79 (*o*-P(O)(C_6H_5)$_2$), 7.47 (*m,p*-P(O)(C_6H_5)$_2$), 2.27 ($-CH_2$P(O)(C_6H_5)$_2$), 2.0−1.0 ($-CH_2-$), 0.97 ($-CH_3$). ^{13}C NMR (101 MHz, $C_2D_2Cl_4$): δ 131.7; 130.7, 128.2, 31.6, 29.4, 22.3, 21.4, 13.5. ^{31}P NMR (202 MHz, $C_2D_2Cl_4$): δ 32.5.

Polymerization of Ethylene in the Presence of Diethylphosphine. Representative Experiment. The same procedure as for the above reaction was employed, except that Cp′$_2$LaCH(SiMe$_3$)$_2$ (2.9 mg, 5.1 μmol) was used as the catalyst and diethylphosphine (0.21 mL, 1.1 mmol) was used as the chain-transfer agent. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 2.4 ($-CH_2$P(O)Et$_2$), 2.0−1.0 ($-CH_2-$), 0.95 ($-CH_3$). ^{31}P NMR (162 MHz, $C_2D_2Cl_4$): δ 52.

Polymerization of Ethylene in the Presence of Diisobutylphosphine. Representative Experiment. The same procedure as for the above reaction was employed, except that diisobutylphosphine (0.21 mL, 1.1 mmol) was used as the chain-transfer agent. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 2.19 ($-CH_2$P(O)^{i}Bu$_2$), 2.0−1.0 ($-CH_2-$), 1.17, 0.98. ^{31}P NMR (162 MHz, $C_2D_2Cl_4$): δ 47.

Polymerization of Ethylene in the Presence of Dicyclohexylphosphine. Representative Experiment. The same procedure as for the above reaction was employed, except that dicyclohexylphosphine (0.13 mL, 1.1 mmol) was used as the chain-transfer agent.^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 2.0−1.0 ($-CH_2-$).

Polymerization of Ethylene in the Presence of Cyclohexylphosphine. Representative Experiment. In the glovebox, a Teflon-valved storage tube, which had been dried overnight on the high-vacuum line (10^{-6} Torr) and equipped with a stir bar, was charged with Cp′$_2$YCH(SiMe$_3$)$_2$ (4.4 mg, 8.5 μmol) and dry toluene (1.0 mL). The storage flask was then attached to the vacuum line, and hydrogen (1.0 atm) was introduced. The precatalyst was stirred under hydrogen (1.0 atm) for 2 h at 20 °C and then stirred for an additional 2 h as a closed system. Next, cyclohexylphosphine (0.115 mL, 0.87 mmol) was added under an argon flush and the mixture stirred at room temperature for 2 h. The yellow catalyst solution was then cooled to −78 °C, and high vacuum was applied to remove trace amounts of hydrogen. In the glovebox, a three-necked Morton flask, which had been dried overnight on a high-vacuum line, 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 ethylene (1.0 atm) was introduced with rapid stirring. The catalyst and phosphine solution were then injected into the reactor with rapid stirring. After 30 min, methanol (10 mL) was injected to quench the reaction. A 10 mL aliquot of the reaction mixture was reserved for analysis. Under Schlenk line vacuum (10^{-3} Torr), the volatile portion of the 10.0 mL aliquot was vacuum-transferred away from the nonvolatile portion. The volatile solution was analyzed by GC−MS, and the nonvolatile portion was analyzed by MALDI-TOF MS. ^{1}H NMR (500 MHz, C_7D_8): δ 6.32 (J_1 = 430, *H*PCy−), 1.75 [HPCyCH_2(CH_2CH_2)$_n$$CH_3$], 1.58 (HP*Cy*), 1.49 (HP*Cy*), 1.1−1.4 ($-CH_2CH_2-$), 1.00 (HP*Cy*), 0.92 ($-CH_3$). ^{13}C NMR (126 MHz, C_7D_8): δ 32.8, 30.7, 30.6, 30.4, 30.3, 30.2, 27.0, 26.8, 26.6, 26.3, 25.6, 23.6, 23.0, 14.8. ^{31}P NMR (162 MHz, C_7D_8): δ 37.8.

Polymerization of Ethylene in the Presence of Phenylphosphine. Representative Experiment. The same procedure as for the above reaction was employed, except that phenylphosphine (0.085 mL, 0.86 mmol) was used as the chain-transfer agent.

Polymerization of Ethylene (without Phosphine). Representative Experiment. In the glovebox, a Teflon-valved storage tube, which had been dried overnight on the high-vacuum line (10^{-6} Torr) and equipped with a stir bar, was charged with Cp′$_2$LaCH(SiMe$_3$)$_2$ (1.4 mg, 2.5 μmol) and dry toluene (1.0 mL). The storage flask was then attached to the vacuum line, and hydrogen (1.0 atm) was introduced. The precatalyst was stirred under hydrogen (1.0 atm) for 2 h at 20 °C and then stirred for an additional 2 h as a closed system. The catalyst solution was cooled to −78 °C, and high vacuum was applied to remove trace amounts of hydrogen. In the glovebox, a three-necked Morton flask, which had been dried overnight on a high-vacuum line, 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 ethylene (1.0 atm) was introduced with rapid stirring. The catalyst solution was then injected into the reactor with rapid stirring. A rapid temperature rise was observed during the polymerization. After 5 s, methanol (5 mL) was injected to quench the reaction. Excess methanol (~400 mL) was then used to precipitate the polymer. The polymer (0.38 g) was collected by filtration, washed with methanol (100 mL) and chloroform (100 mL), and dried in vacuo overnight.

Catalyst Activation Studies. In the glovebox, an NMR tube equipped with a Teflon valve was loaded with Cp′$_2$LaCH(SiMe$_3$)$_2$ (4.8 mg, 8.5 μmol) and C_6D_6 (0.6 mL). On the high-vacuum line, the tube was evacuated while frozen at −78 °C, and diphenylphosphine (0.06 mL, 3.4 μmol) and C_6D_6 (0.2 mL) were added via syringe under an argon flush. The tube was evacuated and backfilled with Ar while frozen at −78 °C, and then the tube was sealed. The frozen reaction mixture was maintained at −78 °C until kinetic measurements were begun. The sample tube was warmed quickly and inserted into the probe of the spectrometer, which had been previously set to 60 °C (temperature calibrated with ethylene glycol standard). ^{1}H NMR data were collected using one scan per interval time and a 45° pulse. Reactions were monitored by measuring the disappearance of the Cp′$_2$LaCH[Si(CH_3)$_3$]$_2$ or (C_5Me_5)$_2$LnCH(SiMe$_3$)$_2$ peak. Protonolysis rate constants, $k_{protonolysis}$, were calculated from the least-squares-determined slope according to eqs 4 and 5.

$$\ln [\text{precatalyst}]_t = \ln [\text{precatalyst}]_0 - k't \tag{4}$$

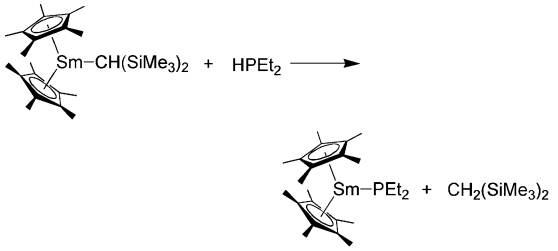
$$k' = k_{\text{protonolysis}}[\text{phosphine}] \tag{5}$$

Results

The goal of this research was to investigate the scope and mechanism of phosphines as electron-rich chain-transfer agents for organolanthanide-mediated olefin polymerization. Previously, we briefly communicated the catalytic synthesis of diphenylphosphine-capped polyethylene.[20] In this contribution, we extend the study to include other secondary phosphines and broaden the scope to include primary phosphines. After a brief discussion of catalyst activation, in the first section we discuss the effectiveness of diphenyl-, dicyclohexyl-, diisobutyl-, diethyl-, phenyl-, and cyclohexylphosphine to function as chain-transfer agents. Next, the effect of phosphine and lanthanide ion on polymerization characteristics will be addressed from a mechanistic standpoint. Intramolecular hydrophosphination/cyclization mechanistic phenomenology will then be used to rationalize some of the present observations and trends. Finally, various aspects of the catalytic cycle will be discussed, including the effect of protonolysis and initiation rate on phosphine chain-transfer efficiency.

Catalyst Activation. The chain termination step of the proposed catalytic cycle (Scheme 2, step iii) involves proto-

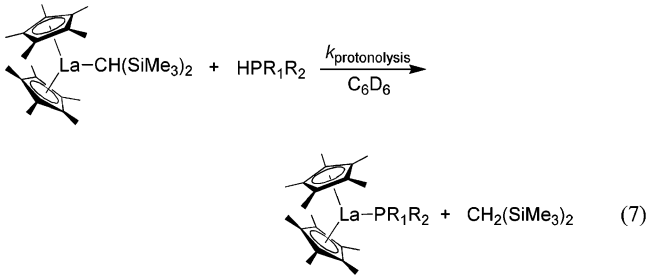
nolysis of an Ln−C σ-bond with concomitant formation of a lanthanide−phosphide σ-bond. This step is doubtless thermodynamically favorable, as evidenced by the analogous exothermic reaction between $Cp'_2SmCH(SiMe_3)_2$ and $HPEt_2$ (eq 6).[23] Depending on the lanthanide ionic radius, phosphine structure, phosphine concentration, and precatalyst concentration, we find that the complete protonolysis requires hours to days at room temperature. It was previously observed that the rate of Ln−C protonolysis by primary alkylphosphines increases with increasing lanthanide ionic radius.[17d] This likely reflects a sterically crowded protonolysis transition state (Scheme 2, transition state **II)**.



(6)

ΔH_{calc} = -7 kcal/mol of Sm

To better understand the crucial chain-transfer/termination step, we investigated the kinetics of intermolecular protonolysis of $Cp'_2LaCH(SiMe_3)_2$ with selected secondary and primary phosphines (eq 7).



(7)

R_1 =	R_1 =
H	Ph
H	Cy
Ph	Ph
Et	Et
^{i}Bu	^{i}Bu
Cy	Cy

$Cp'_2LaCH(SiMe_3)_2$ was contacted with phenyl-, cyclohexyl-, diphenyl-, diethyl-, diisobutyl-, and dicyclohexylphosphine under nearly identical conditions at 60 °C in C_6D_6, and the ensuing protonolysis reactions were monitored as a function of time by ^{1}H NMR (Table 1). The protonolysis reactions occur cleanly, and depending on the details of the phosphine substitution, La−C protonolysis by the various phosphines requires minutes to hours at 60 °C. In the present study, the dependence of protonolysis rate on phosphine was observed to be the following (Table 1):

$$HPCy_2 < HP^iBu_2 \approx HPEt_2 < HPPh_2 \approx H_2PCy \ll H_2PPh$$

If the rates of protonolysis were influenced *only* by phosphine steric properties, the rates would be expected to increase in the following manner (based on Tolman cone angles[24] and MINDO/3 optimized geometries and heats of formation[25]):

$$HPCy_2 < HP^iBu_2 \approx HPPh_2 < HPEt_2 < H_2PCy < H_2PPh$$

Table 1. Effect of Phosphine Substituents on Protonolysis Reaction Time of $Cp'_2LaCH(SiMe_3)_2$

entry	phosphine	[phosphine] (mM)	reaction time[a] (min)	$k_{protonolysis}$[b] (M^{-1} s^{-1})	% conv[c]
1	H_2PPh	290	9	1.6 (0.1)	94
2	H_2PCy	240	70	0.19 (0.01)	96
3	$HPPh_2$	400	70	0.11 (0.01)	95
4	$HPEt_2$	385	110	0.078 (0.009)	92
5	HP^iBu_2	445	100	0.070 (0.012)	96
6	$HPCy_2$	440	170	0.041 (0.018)	95

[a] NMR-scale reaction conditions: 0.8 mL of C_6D_6, 60 °C, organolanthanide concentration = 11 mM. [b] Assuming rate law: $v = k[Ln]^1[phosphine]^1$. [c] Monitored by ^{1}H NMR.

With the exception of diphenylphosphine, the present La−C protonolysis rates are inversely related to increasing phosphine steric bulk; i.e., the rate of protonolysis with primary phosphines is more rapid than that involving secondary phosphines. In addition, dicyclohexylphosphine, the bulkiest phosphine, exhibits the slowest protonolysis rate. However, diphenylphosphine, which is similar in steric bulk to diisobutylphosphine and less bulky than diethylphosphine,[24,25] effects Ln−C protonolysis more rapidly than diethyl- and diisobutylphosphine. The rate of Ln−C protonolysis by diphenylphosphine is similar to the rate observed with cyclohexylphosphine, which is significantly less bulky than diphenylphosphine. Clearly, phosphine steric as well as electronic properties affect the rate of Ln−C protonolysis.

While formation of Cp'_2Ln−phosphido species is sluggish from the hydrocarbyl complex under typical catalytic conditions, formation from the corresponding lanthanocene hydrides occurs within seconds to minutes at room temperature. Therefore, the $Cp'_2LnCH(SiMe_3)_2$ precatalysts were first converted to the corresponding hydrides, $(Cp'_2LnH)_2$, in situ using H_2. Finally, the corresponding lanthanide−phosphido complexes were generated from the lanthanide−hydride complexes upon addition of excess phosphine and used as either isolated or in situ generated catalysts.

Effect of Diphenylphosphine on Lanthanide-Mediated Ethylene Polymerizations. The first phosphine investigated as a chain-transfer agent for organolanthanide-mediated ethylene polymerization was diphenylphosphine (Table 2). All polymerizations were conducted under 1.0 atm ethylene under rigorously anaerobic/anhydrous conditions with $Cp'_2LnCH(SiMe_3)_2$ and $(Cp'_2LnH)_2$ precatalysts ($Cp' = \eta^5$-Me_5C_5)[3] using procedures minimizing mass transport effects,[3] with olefin concentration held constant and the diphenylphosphine concentration maintained in pseudo-zero-order excess. Since polymers would be produced via ethylene insertion into the Ln−P bond, and the phosphine moiety is transferred to the polymer chain at the beginning of the chain growth, Cp'_2LnPPh_2 complexes were first generated prior to polymerization either in situ or as isolated complexes. For ease of handling, all polymer samples were

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(25) DeSanto, J. T.; Mosbo, J. A.; Storhoff, B. N.; Bock, P. L.; Bloss, R. E. *Inorg. Chem.* **1980**, *19*, 3086.

Table 2. Organolanthanide-Catalyzed Ethylene Polymerization in the Presence of Diphenylphosphine

entry	precatalyst[a]	[precat.] (μM)	[$HPPh_2$] (mM)	yield (g)	activity[b] ($\times 10^7$)	T_i[c] (°C)	T_f[d] (°C)	M_n[e]	M_w/M_n[e]	T_m[f] (°C)
1	Cp'_2LuR	79	20	0.25	0.73	18	22	37500	1.6	138
2	Cp'_2YR	78	20	0.70	2.1	18	36	25500	1.9	138
3	Cp'_2SmR	83	20	0.27	0.76	18	24	18900	2.1	137
4	Cp'_2LaR[g]	85	20			17	17			
5	Cp'_2LaR[h]	100	22	0.099	0.0039	17	17	4000	2.0	131
6	Cp'_2YPPh_2	36	22	0.48	3.1	17	25	29500	1.8	138
7	Cp'_2YPPh_2	36	45	0.45	2.9	17	26	18800	2.2	137
8	Cp'_2YPPh_2	39	67	0.48	2.9	17	27	12500	2.3	136
9	Cp'_2YPPh_2	35	89	0.41	2.7	16	24	11000	2.4	135
10	Cp'_2YPPh_2	35	121	0.35	2.3	17	24	9400	2.3	135
11	Cp'_2YPPh_2	35	154	0.23	1.5	17	21	7100	2.3	135
12	Cp'_2YPPh_2	33	418	0.070	0.46	17	19	3100	2.0	130

[a] Cp' = η^5-Me_5C_5, R = $CH(SiMe_3)_2$; polymerization conditions: 50 mL of toluene, 30 s. [b] Units = g/(mol of Ln·atm ethylene·h). [c] Initial temperature. [d] Final temperature. [e] By GPC in 1,2,4-trichlorobenzene vs polyethylene standards. [f] By DSC. [g] Only trace amounts (<10 mg) of polymer are obtained. [h] Polymerization time = 3 min.

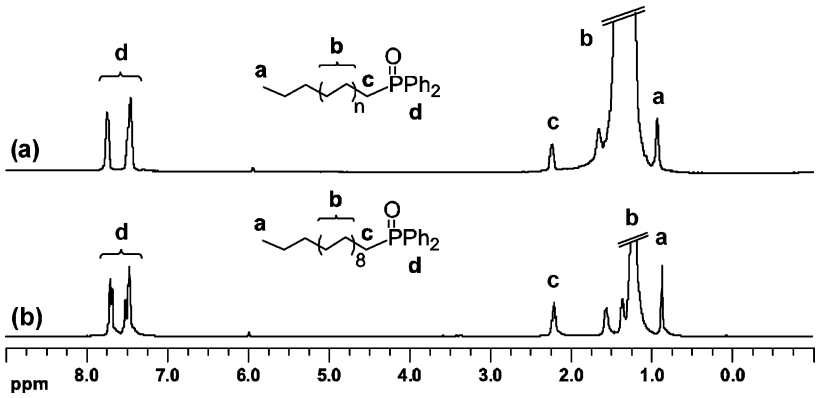
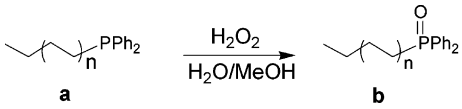


Figure 1. ^1H NMR spectra (500 MHz, $C_2D_2Cl_4$) of (a) diphenylphosphine oxide-terminated polyethylene synthesized by in situ generated Cp'_2YPPh_2 and (b) 1-eicosyldiphenylphosphine oxide.

oxidized to the corresponding phosphine oxide-capped derivatives (eq 8) prior to characterization by ^1H, ^{13}C, and ^{31}P NMR (Figure S-1b).[26]



(8)

The ^1H and ^{13}C NMR spectra of the phosphine-terminated polyethylenes produced by in situ generated Cp'_2YPPh_2 exhibit characteristic phenyl (δ = 7.79, 7.47), polyethylene backbone (δ = 2.0−1.0), $-CH_2P(O)Ph_2$ (δ = 2.27), and $-CH_3$ (δ = 0.97) chain end resonances (Figures 1a and 2a). The concentrations of any vinyl chain end resonances are below the detection limits in both the ^1H and ^{13}C NMR spectra, suggesting that chain transfer/termination via β-H elimination (to metal or monomer) is insignificant, and consistent with the mechanistic scenario of Scheme 2. Furthermore, the ~1:1 PPh_2 and $-CH_3$ chain end resonance ratio implies that a phosphine moiety terminates each polymer chain. The ^1H, ^{13}C, and ^{31}P NMR spectra of the model product 1-eicosyldiphenylphosphine oxide (**2**; Figures 1b and 2b) are in good agreement with the polymer spectral structural assignments.

Regardless of the catalyst lanthanide ionic radius, vinyl resonances are absent in the ^1H NMR spectra of the polymers produced in the presence of diphenylphosphine, which suggests that β-hydride elimination is not a competing chain termination process. In addition, the resulting diphenylphosphine-capped polyethylenes have narrow, monomodal polydispersities and a single resonance in the ^{31}P NMR (δ = 33 ppm), which is consistent with a single-site process.

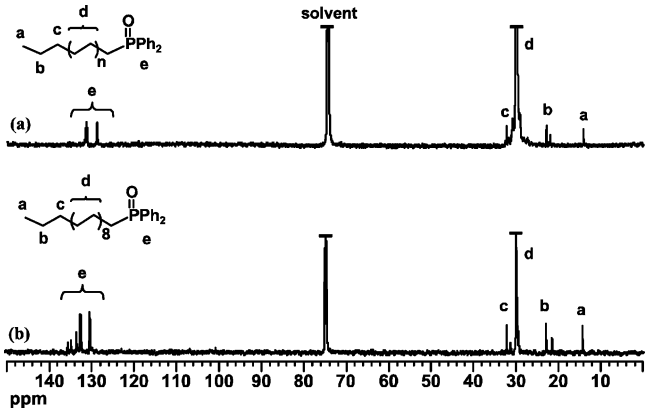


Figure 2. ^{13}C NMR spectrum (126 MHz, $C_2D_2Cl_4$) of (a) diphenylphosphine oxide-terminated polyethylene synthesized by in situ generated Cp'_2YPPh_2 and (b) 1-eicosyldiphenylphosphine oxide (**2**).

With polymerizations conducted in the presence of diphenylphosphine, lanthanide ionic radius and polymer molecular weight are inversely related. Ethylene polymerizations mediated by in situ generated Cp'_2LaPPh_2 in the presence of diphenylphosphine (~20 mM) require relatively high catalyst concentrations and long reaction times (vs the other lanthanide metals) to produce significant amounts of polymer with low molecular weight (M_n = 4000; Table 2, entry 5). On the other hand, polymerizations mediated by smaller lanthanide metals, Sm, Y, and Lu, produce diphenylphosphine-capped polyethylenes with

(26) See Supporting Information for ^{31}P NMR spectrum (Figure S-1).

Table 3. Organolanthanide-Catalyzed Ethylene Polymerization in the Presence of Various Secondary Phosphines

entry	precatalyst[a]	phosphine	[precat.] (μM)	[phos.] (mM)	time (s)	yield (g)	activity[b]	T_i[c] (°C)	T_f[d] (°C)	M_n[e]	M_w/M_n[e]
1	Cp'_2LaR	$HPPh_2$	100	22	1800	0.099	3.9×10^4	17	17	4000	2.0
2	Cp'_2LaR	$HPEt_2$	100	22	30	0.22	5.1×10^6	18	23	14800	2.6
3	Cp'_2LaR	HP^iBu_2	100	22	30	0.90	2.1×10^7	17	36	15300	2.6
4	Cp'_2LaR	$HPCy_2$	98	20	30	0.66	1.6×10^7	17	32	44400	1.6
5	Cp'_2LaR	$HPCy_2$	97	155	30	0.50	1.2×10^7	19	36	47500	1.5
6	Cp'_2YR	$HPPh_2$	98	22	30	0.70	1.7×10^7	17	31	24400	2.0
7	Cp'_2YR	$HPEt_2$	94	22	30	0.71	1.8×10^7	17	28	30200	2.0
8	Cp'_2YR	HP^iBu_2	98	22	30	0.88	2.1×10^7	17	36	25500	2.3
9	Cp'_2YR	$HPCy_2$	98	22	30	0.99	2.4×10^7	18	36	26700	2.2

[a] Cp' = η^5-Me_5C_5, R = $CH(SiMe_3)_2$; polymerization conditions: 50 mL of toluene. [b] Units = g/(mol of Ln·atm ethylene·h). [c] Initial temperature. [d] Final temperature. [e] By GPC in 1,2,4-trichlorobenzene vs polyethylene standards.

Table 4. Organolanthanide-Catalyzed Ethylene Polymerization in the Absence of Phosphine

entry	precatalyst[a]	[cat.] (μM)	time (s)	yield (g)	activity[c]	T_i[d] (°C)	T_f[e] (°C)	M_n[f]	M_w/M_n[f]
1	Cp'_2LaR[b]	48	5	0.38	1.1×10^8	18	29	52300	1.4
2	Cp'_2SmR[b]	44	5	0.29	9.4×10^7	17	25	57000	1.3
3	Cp'_2YH	65	15	0.97	7.8×10^7	16	29	31000	1.9

[a] Cp' = η^5-Me_5C_5, R = $CH(SiMe_3)_2$; polymerization conditions: 50 mL of toluene. [b] Ln−H species generated in situ. [c] units = g/(mol of Ln·atm ethylene·h). [d] Initial temperature. [e] Final temperature. [f] By GPC in 1,2,4-trichlorobenzene vs polyethylene standards.

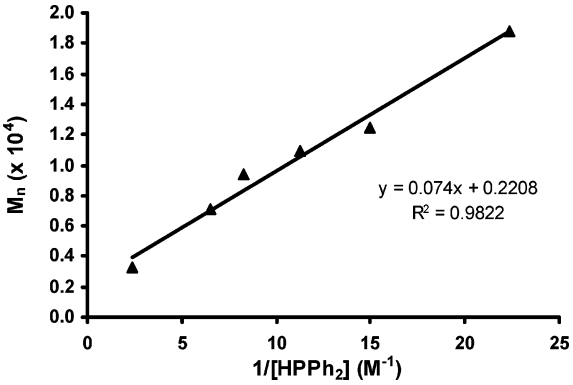


Figure 3. Relationship of diphenylphosphine-capped polyethylene number-average molecular weight (GPC versus polyethylene) to inverse diphenylphosphine concentration at fixed catalyst and ethylene concentrations.

higher molecular weights (10^4) and surprisingly high activities (10^7 g of polymer/(mol of Ln·atm ethylene·h)). In fact, polymerization activities observed with Cp'_2YPPh_2 are not greatly depressed over a ~20-fold increase in diphenylphosphine concentration (Table 2) and may be influenced by trace impurities in the phosphine (catalyst poisoning) at very high phosphine concentrations. Furthermore, at constant Cp'_2YPPh_2 and ethylene concentrations, product polyethylene molecular weight is inversely proportional to phosphine concentration (Table 2, entries 6−12; Figure 3), supporting the chain-transfer mechanism shown in Scheme 2. Additional mechanistic discussion is presented below.

Diethylphosphine as a Chain-Transfer Agent for Ethylene Polymerization. The secondary phosphines diethylphosphine, dicyclohexylphosphine, and diisobutylphosphine were also investigated as chain-transfer agents for ethylene polymerization using $Cp'_2LnCH(SiMe_3)_2$ lanthanocene precatalysts (Ln = La, Y; Table 3). As noted above, with ethylene polymerizations in the presence of diphenylphosphine, high polymerization activities are observed in the presence of all three dialkylphosphines. In addition, it can be seen that the product polymers have narrow polydispersities, which is consistent with a single-site mechanism.

Ethylene polymerizations were carried out in the presence of 22 mM diethylphosphine using $Cp'_2LnCH(SiMe_3)_2$ (Ln = La, Y) as precatalysts (Table 3; entries 2 and 7). In situ generated Cp'_2LaPEt_2 is orange while the corresponding alkyls and hydrides are colorless, and during the course of the polymerization the reaction solution remains orange, which suggests the presence of La−P species. The ^{1}H NMR spectra of the diethylphosphine oxide-terminated polyethylenes produced by in situ generated Cp'_2LaPEt_2 exhibit characteristic $-CH_2P(O)Et_2$ (δ = 2.4 ppm), polyethylene (δ = 1.3 ppm) backbone, and $-CH_3$ (δ = 0.95 ppm) chain end resonances (Figure S-2).[27] Furthermore, the ~1:1 $CH_3(CH_2CH_2)_nCH_2P(O)Et_2$ and $CH_3(CH_2CH_2)_nCH_2P(O)Et_2$ chain end ratios and absence of vinyl resonances imply that a phosphine moiety terminates each polymer chain and that β-hydride chain-transfer processes are minimal. A single ^{31}P NMR resonance (δ = 52 ppm) and narrow monomodal polydispersity also suggest a single-site mechanism as in Scheme 2.

The ^{1}H NMR spectrum of polymer produced by in situ generated Cp'_2YPEt_2 also exhibits a characteristic $CH_3(CH_2CH_2)_nCH_2P(O)Et_2$ signal at δ = 2.4 ppm; however, due to the higher molecular weight of the Cp'_2Y-derived polymer, the $-CH_3$ terminus cannot be readily distinguished from the polymer backbone, and the ratio of $-CH_3$ termini to $-CH_2P(O)Et_2$ termini cannot be accurately assayed. A single ^{31}P NMR $-CH_2P(O)Et_2$ resonance at δ = 52 ppm and narrow monomodal polydispersity suggest a single-site mechanism. The molecular weight of the polymer produced by the Cp'_2YPEt_2-mediated polymerization (Table 3, entry 7) is not significantly less than the polyethylene M_n produced by $[Cp'_2YH]_2$ in the absence of phosphine (Table 4, entry 3). While it cannot be determined whether 100% of the polyethylene chains are capped by a phosphine moiety, the lack of detectable vinyl resonances in the ^{1}H NMR spectra argues that β-hydride elimination is not a significant termination/chain-transfer pathway, and that Scheme 2 is the predominant pathway.

Diisobutylphosphine as a Chain-Transfer Agent for Ethylene Polymerization. Ethylene polymerizations were carried

(27) See Supporting Information for ^{1}H NMR spectrum (Figure S-2).

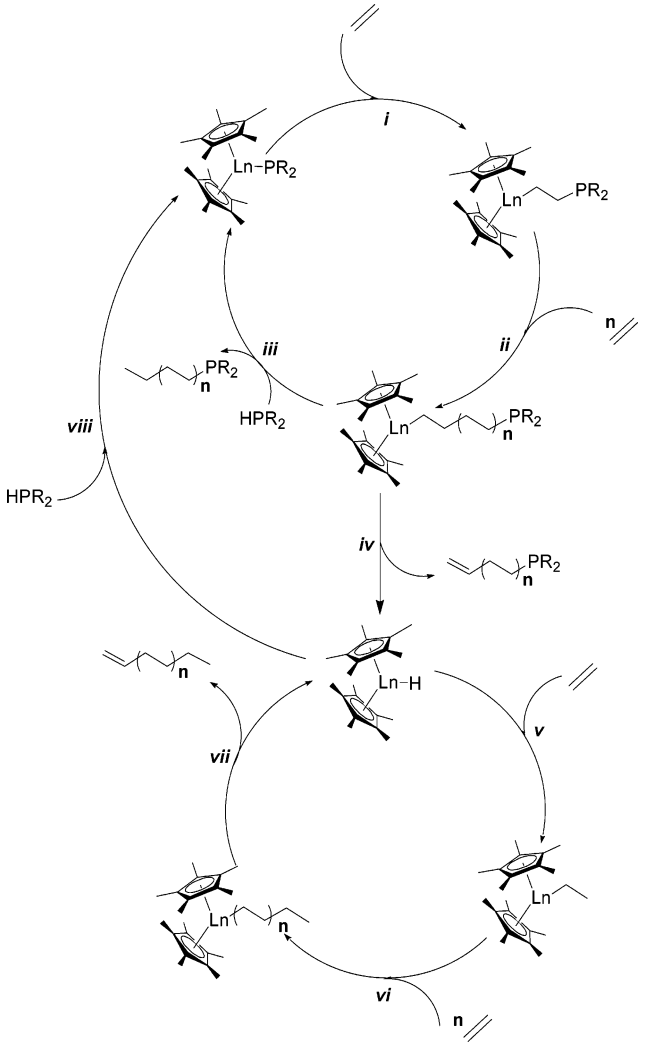
out in the presence of 22 mM diisobutylphosphine using $Cp'_2LnCH(SiMe_3)_2$ (Ln = La, Y) as precatalysts (Table 3, entries 3 and 8). In situ generated $Cp'_2LaP^iBu_2$ is orange in color, and during the course of the polymerization the reaction solution remains yellow-orange, which implies the presence of a La−P species. The ^{1}H NMR spectrum of the polyethylene produced by in situ generated $Cp'_2LaP^iBu_2$ exhibits characteristic $-CH_2P(O)^iBu_2$ (δ = 2.2 ppm), $-CH_2P(O)[CH(CH_3)_2]_2$ (δ = 1.17 ppm), polyethylene backbone (δ = 1.4 ppm), and $-CH_3$ (δ = 0.96 ppm) chain end resonances (Figure S-3).[28] All other isobutyl resonances overlap with the polyethylene backbone. The ~1:1 $-CH_2P(O)^iBu_2$ and $-CH_3$ chain end resonance ratio and absence of vinyl resonances suggest that a phosphine moiety terminates each polymer chain. The narrow monomodal polydispersity and a single ^{31}P NMR resonance (δ = 47 ppm) also suggest a single-site pathway.

Ethylene polymerizations were conducted with in situ generated $Cp'_2YP^iBu_2$ in the presence of 22 mM diisobutylphosphine. In situ generated $Cp'_2YP^iBu_2$ is orange, and after injection of the catalyst solution into the reaction flask, the reaction solution becomes essentially colorless and remains so during the course of the polymerization, suggesting that any Y−P species, which would be orange, are not present in large quantities. The ^{1}H NMR spectrum of the product polymer exhibits a relatively small $-CH_2P(O)^iBu_2$ resonance (δ = 2.2 ppm); however, this peak as well as that of the methyl terminus overlaps with the polyethylene backbone resonance and cannot be accurately integrated. In addition, vinyl resonances at $\delta \approx$ 5.0 and 5.9 ppm are present, which indicates that β-hydride elimination to metal or monomer (Scheme 3, steps iv and vii) is a significant competing chain termination process.[29] The polyethylene produced by in situ generated $Cp'_2YP^iBu_2$ in the presence of 22 mM diisobutylphosphine has a molecular weight (M_n = 25 500; Table 3, entry 8) that is not significantly less than that of the polymer produced in the absence of phosphine (M_n = 31 000; Table 4, entry 3). Therefore, in ethylene polymerizations mediated by $Cp'_2YP^iBu_2$, the rate of diisobutylphosphine chain transfer does not appear to be competitive with other chain termination pathways.

Dicyclohexylphosphine as a Chain-Transfer Agent for Ethylene Polymerization. Ethylene polymerizations mediated by in situ generated Cp'_2YPCy_2 and Cp'_2LaPCy_2 in the presence of dicyclohexylphosphine appear to be unaffected by the presence of the dicyclohexylphosphine chain-transfer agent (Table 3, entries 4, 5, and 9). In situ generated Cp'_2LaPCy_2 and Cp'_2YPCy_2 solutions are distinctively colored, orange and orange-pink, respectively; however, the reaction solutions become and remain colorless during the course of subsequent ethylene polymerizations. This suggests qualitatively that Ln−P species are not present in significant quantities for either lanthanocene complexes.

Furthermore, polymerizations mediated by Cp'_2LaPCy_2 in the presence of 22 and 155 mM dicyclohexylphosphine (Table 3, entries 4 and 5) yield polymers with indistinguishable molecular weights (M_n = 44 400 and 47 500, respectively), similar to that observed in the absence of phosphine (M_n = 52 300; Table 4, entry 1). That a 7-fold increase in dicyclohexylphosphine concentration does not result in a significant decrease in polymer molecular weight also suggests that the rate of phosphine chain transfer is not competitive with other chain termination pathways, doubtless reflecting the pronounced steric encumbrance of this phosphine. Unfortunately, the polymer molecular weight is too high to allow informative end group analysis by NMR.

Scheme 3. Proposed Catalytic Cycle for Organolanthanide-Catalyzed Ethylene Polymerization in the Presence of Phosphine with Competing Chain Termination via β-Hydride Transfer to Metal



The polyethylene produced by in situ generated Cp'_2YPCy_2 in the presence of 22 mM dicyclohexylphosphine has an M_n = 26 700 (M_w/M_n = 2.2; Table 3, entry 9), which is not significantly less than that of the polymer produced in the absence of phosphine (Table 4, entry 3). The ^{1}H NMR spectrum of the polymer exhibits a relatively weak $-CH_2P(O)Cy_2$ resonance (δ = 2.4 ppm); however, this peak as well as that of the methyl terminus overlaps with the polyethylene backbone resonance and cannot be accurately integrated. The presence of significant vinyl resonances at $\delta \approx$ 5.0 and 6.0 ppm indicates that β-hydride elimination is a major chain termination process and that phosphine chain transfer is not likely to be the dominant termination pathway.

Primary Phosphines as Chain-Transfer Agents for Ethylene Polymerization. We additionally investigated the ef-

(28) See Supporting Information for ^{1}H NMR spectrum (Figure S-3).
(29) A peak at δ47 ppm is observed in the ^{31}P NMR; therefore, it is likely that some of the polyethylene is termined by diisobutylphosphine. However, the presence of vinyl end groups in the ^{1}H NMR argues that phosphine chain transfer is not the dominant termination pathway.

ficiency of the primary phosphines, phenylphosphine and cyclohexylphosphine, as chain-transfer agents for organolanthanide-mediated ethylene polymerizations. In situ generated Cp'_2YPHCy and Cp'_2YPHPh solutions are yellow and orange-yellow, respectively, and these characteristic colors are observed during turnover, which in the case of both phosphines suggests the presence of Y−P species. In the presence of phenylphosphine and cyclohexylphosphine (17 mM), ethylene polymerizations mediated by the $Cp'_2YCH(SiMe_3)_2$ precatalyst failed to produce any methanol-insoluble high-molecular-weight polymer (polymerization time = 30 s). Therefore, the polymerizations were conducted over longer polymerization times (30 min) and at higher catalyst concentrations (∼165 μM) than the polymerizations conducted in the presence of secondary phosphines.

Ethylene polymerizations mediated by $Cp'_2YCH(SiMe_3)_2$ in the presence of cyclohexylphosphine (17 mM, polymerization time = 30 min, 50.0 mL of toluene) result in only trace amounts of methanol-insoluble polymer. Therefore, the polymerizations were terminated with a measured volume of methanol (10 mL), and a 10 mL aliquot of the reaction solution (total volume = 61 mL) was then utilized for MALDI-TOF MS and GC−MS analysis. Since highly volatile compounds cannot be analyzed using MALDI-TOF MS, the volatile fraction of the reserved 10 mL aliquot was vacuum-transferred (10^{-3} Torr) away from the nonvolatile fraction and analyzed using GC−MS. The residual ∼16 mg of white, waxy, nonvolatile residue was collected and analyzed by MALDI-TOF MS. The functional group in the present polyethylenes is the phosphine end group, while for other polyolefins a vinyl end group is usually sufficient for MALDI-TOF detection.[30] Analysis of the nonvolatile fraction revealed a distribution of oligomers with molecular weights corresponding to oligoethylenes singly capped by a cyclohexylphosphine (or cyclohexylphosphine oxide) moiety (Figure 4a) on one end and a $-CH_3$ group on the other. Peaks corresponding to oligomers ranging from $\sim M_2$ to M_{20} (M_i = molecular weight of oligomer with a cyclohexylphosphine group on one end and $-CH_3$ group on the other end of the polymer chain; i = degree of oligomerization, number of ethylene units) were detected. The peak spacing corresponds to the molecular weight of an ethylene monomer unit. The oligomers were not deliberately oxidized to the corresponding phosphine oxide-capped oligomers prior to MALDI-TOF MS analysis. However, since the polymer samples are worked-up and stored under air, partial oxidation by O_2 occurs, and $M_i + 16$ peaks are present which represent phosphine oxide-capped polyethylene (see Figure 4b). No vinyl end group resonances are present in the ^1H and ^{13}C NMR spectra of the nonvolatile fraction, which suggests that phosphine chain transfer is the dominant termination pathway. The volatile fraction of the polymerization mixture was analyzed by GC−MS, and short-chain oligomers were not detected.[31]

Ethylene polymerizations mediated by $Cp'_2YCH(SiMe_3)_2$ in the presence of phenylphosphine (17 mM, polymerization time = 30 min) failed to produce methanol-insoluble polymers. Therefore, a 10.0 mL aliquot of the reaction mixture was analyzed as described above. Only trace amounts of a nonvolatile residue were collected, and no oligomers were detected when analyzed by MALDI-TOF mass spectrometry. GC−MS analysis of the volatile fraction reveals the presence of phenylphosphine, ethylphenylphosphine, and their oxidized counterparts (phenylphosphine oxide and ethylphenylphosphine oxide, respectively). The ethylphenylphosphine product suggests insertion of a single ethylene monomer into the lanthanide−phosphorus bond, followed by Ln−C protonolysis by incoming phenylphosphine (eq 9). However, since higher molecular weight oligomers are not detected, subsequent ethylene insertion is not competitive with protonolytic phosphine chain transfer.

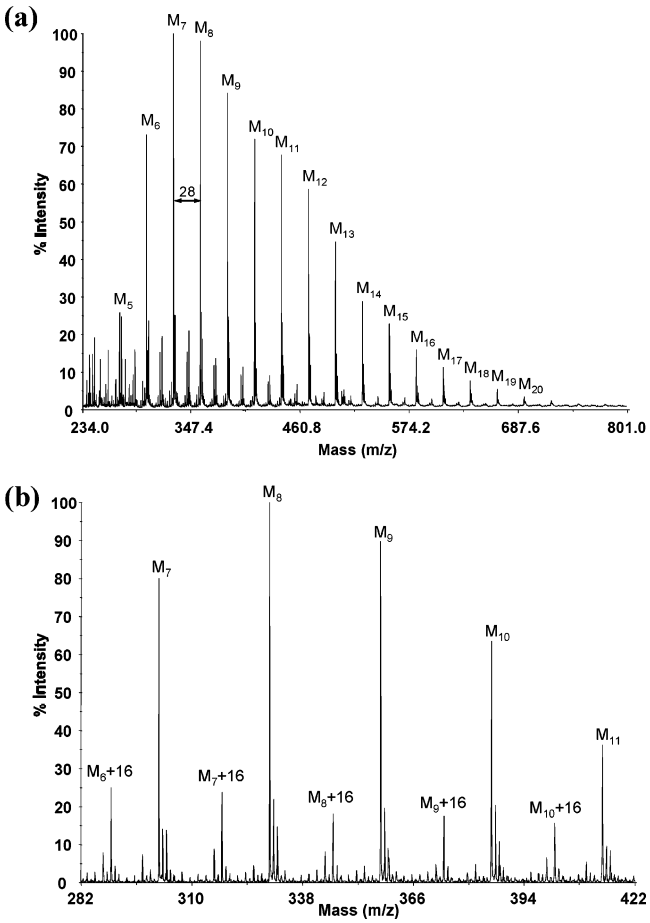
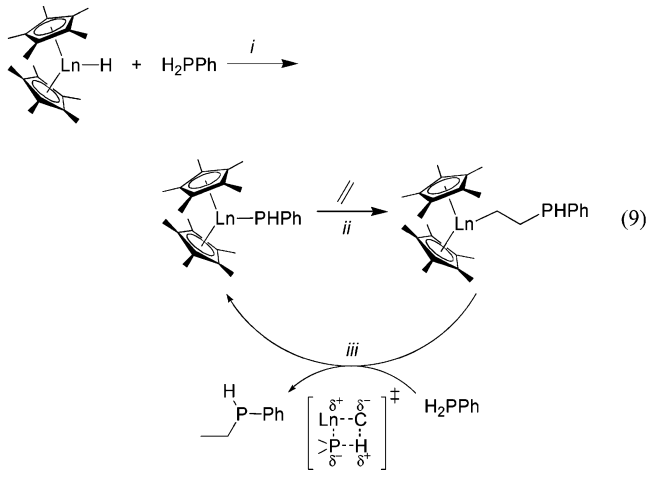


Figure 4. (a)MALDI-TOF mass spectrum of $Cp'_2YCH(SiMe_3)_2$-mediated ethylene polymerization products in the presence of cyclohexylphosphine. (b) Expanded m/z = 282−422 region.



(9)

(30) (a) Janiak, C.; Lange, K. C. H.; Marquadt, P.; Krüger, R.-P.; Hanselmann, R. *Macromol. Chem. Phys.* **2002**, *203*, 129. (b) Wahner, U. M.; Brüll, R.; Pasch, H.; Raubenheimer, H. G.; Sanderson, R. *Angew. Makromol. Chem.* **1999**, *270*, 49.

(31) The formation of cyclic products was not observed by NMR spectroscopy or MALDI-TOF MS.

Summary of the Scope of Phosphine Chain Transfer in Lanthanocene-Mediated Ethylene Polymerization. Cp'_2LnPR_2 (Ln = La, Sm, Y, Lu) complexes mediate the polymerization of ethylene with high activity in the presence of secondary phosphines. However, the synthesis of *phosphine-terminated* polyethylene is highly dependent upon both the phosphine and lanthanide ion employed. For example, regardless of lanthanide identity, phosphine chain transfer does not appear to be efficient in polymerizations conducted in the presence of sterically encumbered dicyclohexylphosphine. Cp'_2LnPCy_2-mediated (Ln = La, Y) polymerizations conducted in the presence of dicyclohexylphosphine produce high-molecular-weight polyethylenes largely devoid of phosphine end groups. However, diethylphosphine is found to be an efficient chain-transfer agent for Cp'_2LaPR_2-mediated ethylene polymerizations. Addition of diethylphosphine to Cp'_2YPEt_2-mediated polymerizations results in depressed polymer molecular weights; moreover, the absence of vinyl resonances in the ^{1}H NMR spectrum additionally suggests that β-hydride elimination is not a competing termination process and that phosphine chain transfer/termination is likely the dominant pathway. While diisobutylphosphine is an efficient chain-transfer agent for Cp'_2LaPR_2-mediated polymerizations, the presence of vinyl resonances in the ^{1}H NMR spectrum of Cp'_2YPR_2-produced polymer suggests that β-hydride elimination is competitive with phosphine chain transfer/termination. In contrast, diphenylphosphine, regardless of the lanthanocene catalyst employed, acts as an efficient chain-transfer agent for ethylene polymerizations. Even polymerizations mediated by Cp'_2Lu-, the smallest lanthanide ion, result in products where diphenylphosphine chain transfer is the dominant termination pathway, with each polymer chain terminated by a phosphine moiety. Cp'_2YPHR-mediated (R = Cy, Ph) ethylene polymerizations conducted in the presence of cyclohexylphosphine or phenylphosphine fail to produce significant amounts of methanol-insoluble polyethylene. Polymerizations conducted in the presence of phenylphosphine and cyclohexylphosphine produce ethylphenylphosphine and methanol-soluble cyclohexylphosphine-capped oligomers ($M_n \approx 350$), respectively.

Discussion

Catalyst Activation as a Function of Phosphine Substitution. The termination step of the proposed catalytic chain growth cycle involves intermolecular lanthanide−carbon bond protonolysis by phosphine (Scheme 2, step iii), which was further investigated by monitoring, as a function of time, the protonolysis reaction of $Cp'_2LaCH(SiMe_3)_2$ with the phosphines investigated in this paper. It is reasonable to assume that the rate of protonolysis is first-order in both phosphine and catalyst concentration. Since the protonolysis reactions were conducted with the phosphine concentration held in pseudo-zero-order excess, the protonolysis rate law can be expressed as eq 10, where $k' = k_{\text{protonolysis}}$[phosphine] (eq 5), and the protonolysis rate constants can be determined by plotting ln[precatalyst] versus time.

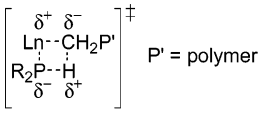
$$\nu = k'[\text{precatalyst}]^1 \qquad (10)$$

The dependence of protonolysis rate $k_{\text{protonolysis}}$ on phosphine (Table 1) is found to be the following:

$$HPCy_2 < HP^iBu_2 \approx HPEt_2 < HPPh_2 \approx H_2PCy \ll H_2PPh$$

Diphenylphosphine, which has approximately the same steric bulk as diisobutylphosphine and is much bulkier than diethylphosphine, affects Ln−C protonolysis at a rate comparable to that of cyclohexylphosphine. Thus, phosphine steric characteristics alone do not account for the observed trend in protonolysis rates.

Diphenylphosphine is no doubt more Brønsted acidic[32] and less Lewis basic[27,33] than diethyl, diisobutyl-, and dicyclohexylphosphine. The electron-withdrawing properties of the phenyl groups and increased Brønsted acidity of diphenylphosphine should stabilize the four-centered σ-bond metathesis transition state (**II**), in comparison to the dialkylphosphines. On the other hand, diphenylphosphine is less Lewis basic than the dialkylphosphines, which, a priori, would seem to favor coordination of dialkylphosphines to the Lewis acidic lanthanide ions over diphenylphosphine. However, since the rate of Ln−C protonolysis is more rapid with diphenylphosphine than with either diethyl or diisobutylphosphine, it appears that Brønsted acidity plays the more significant role in the phosphine chain-transfer transition state. The consequences for olefin polymerization processes are discussed below.



II

Effect of Phosphine Steric and Electronic Properties on Ethylene Polymerization. The present results indicate that the effectiveness of phosphine chain transfer in lanthanocene-mediated ethylene polymerization decreases in the order

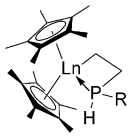
$$H_2PPh \gg H_2PCy > HPPh_2 > HPEt_2 \approx HP^iBu_2 > HPCy_2$$

This trend is identical to that discussed above in rates of lanthanum−carbon σ-bond protonolysis by the same phosphines, suggesting that the overall efficiency of phosphine capping is largely governed by, and chain growth largely limited by, the rate of protonolytic Ln−C cleavage (Scheme 2, step iii).

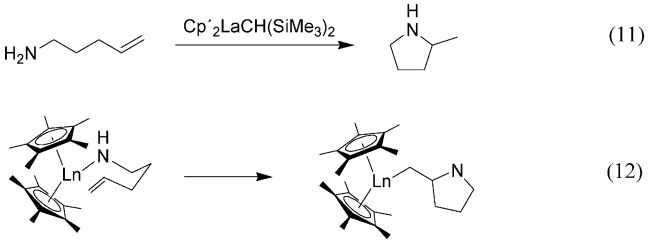
Unlike lanthanocene-mediated polymerizations conducted in the presence of secondary phosphines, polymerizations conducted under the present conditions in the presence of primary phosphines produce only monoethylene insertion products or phosphine-capped oligomers in the case of phenylphosphine and cyclohexylphosphine, respectively. This is consistent with the observation that $Cp'_2LnCH(SiMe_3)_2$ protonolysis is rapid in the presence of primary phosphines. It was previously observed in systems involving thiophene and pyridine that the monoinsertion products, $Cp'\overline{LnCH_2CH_2(C_4H_3S)}$ (Ln = Y, La)[12] and $Cp'\overline{YCH_2CH_2(2\text{-}C_5H_4N)}$,[15] respectively, are particularly stable toward further ethylene insertion. Therefore, it is possible in the present systems that the monoinsertion product, $Cp'_2YCH_2CH_2PHPh$, is less reactive toward subsequent ethylene insertion due to intramolecular phosphine coordination to the lanthanide metal center (e.g., **III**). DFT studies investigating the geometries and

(32) (a) Hudson, H. R. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley and Sons: New York, 1990; Vol. 4, pp 473−487. (b) Issleib, K.; Kümmel, R. *J. Organomet. Chem.* **1965**, *3*, 84.
(33) (a) Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681. (b) Allman, T.; Goel, R. G. *Can. J. Chem.* **1982**, *60*, 716. (c) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985. (d) Henderson, W. A.; Streuli, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791.

stabilities of the intermediates and transition states for organolanthanide-catalyzed hydroamination/cyclization of 1-aminopent-4-ene (eq 11) find two stable conformations, **IV** and **V**, as products following intramolecular insertion of the olefin into the La−N bond (eq 12).[34]



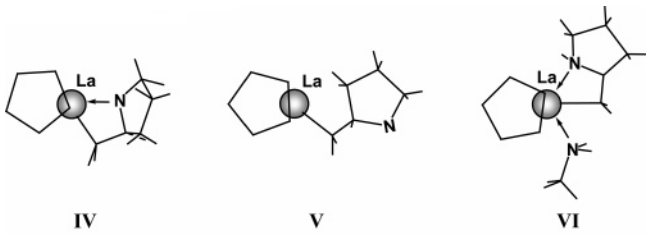
III



(11)

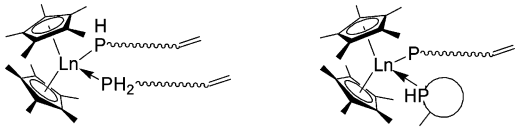
(12)

Conformation **IV**, which involves coordination of the cyclic amine to the lanthanum center, is 16.4 kcal/mol more stable than conformation **V**. This provides evidence that monoinsertion product **III** may indeed be stabilized by phosphine coordination to the electrophilic lanthanide center. Further hydroamination calculations reveal that additional *intermolecular* coordination of an amine (modeled as a methylamine) brings about an additional ∼17 kcal/mol stabilization in affording amine−amido complex **VI**.[29]



IV **V** **VI**

DFT calculations performed on the analogous lanthanocene-catalyzed phosphinoalkene hydrophosphination/cyclization system yield similar findings.[35] In addition, experimental intramolecular phosphinoalkene hydrophosphination/cyclization results suggest that the probable catalyst resting state is a mixture of phosphine−phosphido species **VII** and **VIII**.[17c,d]



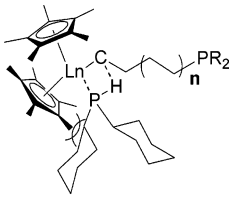
VII **VIII**

Therefore, for ethylene polymerizations involving primary phosphines, further stabilization may be obtained via either intra- and/or intermolecular phosphine coordination. Of course, the additional coordination of one or more phosphines to the metal center would likely impede ethylene coordination/activation, thereby disfavoring enchainment and, in the case of intermolecular phosphine coordination, favoring protonolytic chain transfer. The stability of this additional phosphine coordination is expected to be greatest for the largest Ln ions.

Unlike the lanthanocene polymerizations conducted in the presence of primary phosphines, ethylene polymerizations conducted in the presence of secondary phosphines result in relatively high molecular weight polyethylenes (Tables 2 and 3). This likely reflects the increased steric bulk of the secondary phosphines, where it is plausible that the steric repulsions in the monoinsertion product make intramolecular (**IX**) and intermolecular (**X**) coordination of the phosphine to the lanthanide metal center less favorable than in the case of primary phosphines.

IX **X**

In the aforementioned case of ethylene polymerizations conducted in the presence of diphenylphosphine, phosphine chain transfer is the dominant chain termination pathway, regardless of the lanthanide ion employed (Ln = Lu, Y, Sm, La). In comparison, diisobutyl- and diethylphosphine are efficient chain-transfer agents for Cp'_2La- but not for Cp'_2Y-mediated polymerizations, and dicyclohexylphosphine is not an effective chain-transfer agent for either Cp'_2La- or Cp'_2Y-mediated polymerizations. In addition, the polyethylenes produced in the presence of diphenylphosphine have the lowest molecular weights in comparison to polymers produced in the presence of the other secondary phosphines. These results indicate that, among the secondary phosphines, diphenylphosphine is the most efficient chain-transfer agent for lanthanocene-mediated ethylene polymerization. This is consistent with the fact that the rate of $Cp'_2Ln-CH(SiMe_3)_2$ protonolysis is more rapid with diphenylphosphine than with the other secondary phosphines (vide supra). Among the secondary phosphines investigated, diphenylphosphine is sterically intermediate-sized; therefore, the superior efficiency of diphenylphosphine as a chain-transfer agent for ethylene polymerization appears to reflect a combination of both steric and electronic factors. As previously mentioned, it is likely that the increased $HPPh_2$ Brønsted acidity facilitates the chain-transfer process. Since the dialkylphosphines, diethyl- and diisobutylphosphine, are effective chain-transfer agents for Cp'_2La-mediated ethylene polymerizations, electronic considerations alone would argue that dicyclohexylphosphine should be an effective chain-transfer agent as well for Cp'_2La-mediated polymerizations. That dicyclohexylphosphine does not act as an efficient chain-transfer agent suggests that steric encumbrance generates severe nonbonded interactions in chain-transfer transition state **XI**.



XI

(34) Motta, A.; Lanza, G.; Fragalà, I. L.; Marks, T. J. *Organometallics* **2004**, *23*, 4097.
(35) Motta, A.; Fragalà, I. L.; Marks, T. J. Manuscript in Preparation.

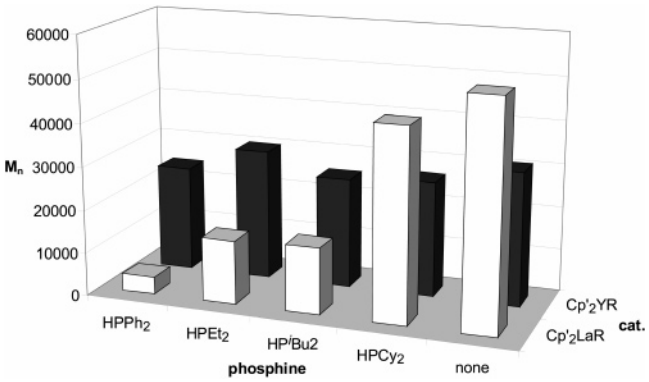


Figure 5. Dependence of polyethylene M_n on phosphine chain-transfer agent and catalyst.

Effect of Lanthanide Ionic Radius on Chain Transfer. In the present polymerization systems, where phosphine chain transfer is the dominant chain-transfer pathway, as is the case with diphenylphosphine, polymer M_n increases with decreasing lanthanide ionic radius. This trend most likely reflects steric constraints in the growth-limiting chain-transfer process (Scheme 2, step iii), involving a relatively crowded transition state (**II**). Consistent with these results is the aforementioned observation, for lanthanide-mediated hydrophosphination, that Ln−C protonolysis is more rapid for larger metal radii.[17d] Furthermore, the metal ionic radius−polymerization activity trend for diphenylphosphine-capped polyethylene synthesis is similar to that observed for intramolecular phosphinoalkene hydrophosphination/cyclization, where olefin insertion into a Ln−P bond is turnover limiting:[17d] Y > Lu, Sm > La.

It is not surprising that, in cases where phosphine chain transfer is not the dominant termination pathway (Scheme 3), lanthanide ionic radius−product molecular weight trends parallel those observed in the absence of phosphine (Table 4). Thus, chain termination by β-hydride elimination (Scheme 3, steps iv and vii) would generate a lanthanocene-hydride—an extremely active ethylene polymerization catalyst.[3] The polyolefin produced by a Ln−H species should be essentially identical to that produced at low phosphine concentrations. For example, dicyclohexylphosphine is an inefficient chain-transfer agent for either Cp'_2Y- or Cp'_2La-mediated ethylene polymerizations, and accordingly, the polyethylene produced by $Cp'_2LaPCy_2 + HPCy_2$ has a higher molecular weight than does the polymer produced by $Cp'_2YPCy_2 + HPCy_2$ (Figure 5)—the same trend observed in the absence of phosphines. Cp'_2LaPR_2-mediated polymerizations involving diisobutyl- and diethylphosphine produce polymers having lower molecular weights than the polymer produced by Cp'_2YPR_2, which is understandable since diisobutyl- and diethylphosphine act as efficient chain-transfer agents in the Cp'_2La-mediated systems, thereby significantly depressing the product polyethylene molecular weight. However, for Cp'_2Y-mediated polymerizations, the rate of diisobutylphosphine phosphine chain transfer is not competitive with that of other chain-transfer processes.

These results suggest that, in the case of secondary phosphines, the chain-transfer process involves a crowded transition state, which is very sensitive to the steric demands of the metal center. Thus, Cp'_2La-, with a more open coordination sphere around the catalytic center, favors phosphine chain transfer, while the Cp'_2Y- center clearly presents unfavorable steric interactions, rendering protonolysis with secondary alkylphosphines inefficient vs other chain-transfer pathways. As previously noted, it is also possible that a more open coordination sphere around the metal center more readily accommodates intra- or intermolecular phosphine coordination, which should favor chain transfer and disfavor ethylene insertion. Unfortunately, neither Cp'_2La- nor Cp'_2Y- is sterically open enough to accommodate the steric bulk of dicyclohexylphosphine in the chain-transfer transition state **XI**.

With Cp'_2La-mediated polymerizations, secondary phosphine substitution has a large effect on the resulting polymer molecular weight (Figure 5). In comparison, for Cp'_2Y-mediated polymerizations, product polymer molecular weights are fairly invariant to phosphine substitution, arguing that phosphine chain transfer is more effective in Cp'_2La-mediated polymerizations due to the more open coordination sphere.

Kinetics and Mechanism of Organolanthanide-Catalyzed Phosphine-Capped Polyethylene Synthesis. The system $Cp'_2YPPh_2 + HPPh_2$ produces diphenylphosphine-capped polyethylenes over a wide range of phosphine concentrations (Table 2, entries 7−12). A series of polymerizations with varying diphenylphosphine concentrations (in pseudo-zero-order excess) was conducted using Cp'_2YPPh_2 as the catalyst and with constant catalyst and ethylene concentrations. A linear relationship between M_n and 1/[diphenylphosphine] is observed (Figure 3), consistent with diphenylphosphine acting as the dominant chain-transfer agent (see below for additional discussion). As discussed above, the absence of vinyl resonances in the ^{1}H NMR and the ∼1:1 PPh_2:−CH_3 terminus ratios also implicate phosphine chain transfer as the dominant chain-transfer pathway.

Under steady-state conditions, the number average degree of polymerization, P_n, is equal to the rate of propagation, R, divided by the sum of the rates of competing chain-transfer pathways, $\sum R_t$ (eq 13).[36] Assuming a single dominant chain-transfer process by phosphine and rapid chain reinitiation after chain transfer, P_n is given by eq 14, where k_p is the propagation rate constant and k_{phos} the phosphine chain-transfer rate constant.

$$P_n = \frac{R}{\sum R_t} \tag{13}$$

$$P_n = \frac{k_p[\text{olefin}]}{k_{phos}[\text{phos}]} \tag{14}$$

Using this equation and the data shown in Figure 3, we estimate that $k_p/k_{phos} \approx 200$.[37−39] For $[Cp'_2SmH]_2$-mediated ethylene polymerizations conducted in the presence of silane chain-transfer agent $PhSiH_3$, a similar ratio is observed, $k_p/k_{Si} \approx 190$.[13] That this system is well-behaved in a single-site polymerization context and that this analysis is appropriate are supported by the aforementioned high observed polymerization rates, product molecular weights, and polydispersities ≈ 2.0. This model is further supported by the fact that the phosphine chain-transfer efficiency (M_n) and the rate of lanthanum−carbon bond protonolysis follow the same trend (see below), indicating that

(36) Kissin, Y. V. *Isospecific Polymerization of Olefins*; Springer-Verlag: New York, 1985; pp 1−93.
(37) [Ethylene] = 0.19 M. For ethylene solubility data in toluene see: Wang, B. P. Ph.D. Dissertation, University of Massachusetts, 1989.
(38) Allen, P. E. M.; Patrick, C. R. *Kinetics and Mechanisms of Polymerization Reactions*; Halsted Press: New York, 1974; pp 128−149.
(39) That the M_n intercept at infinite [diphenylphosphine] is nonzero appears to reflect the imprecision of GPC-derived data for such low polyethylene molecular weights.

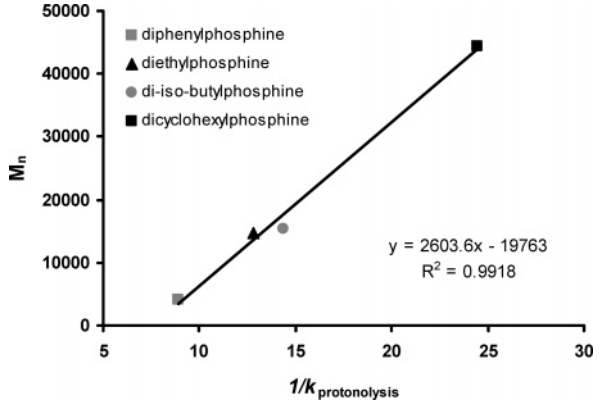


Figure 6. Number-average molecular weight (GPC versus polyethylene) of polyethylene produced by Cp'_2LaPR_2 in the presence of various phosphines versus the rate of $Cp'_2LaCH(SiMe_3)_2$ protonolysis by the corresponding phosphine.

product molecular weight is predominantly governed by the interplay of chain-transfer rate vs that of propagation.

A series of Cp'_2La-mediated ethylene polymerizations was conducted in the presence of selected secondary phosphines (20−22 mM; Table 3, entries 1−4) with constant catalyst, olefin, and phosphine concentrations. Interestingly, when M_n is plotted versus $1/k_{protonolysis}$ for $Cp'_2Ln-CH(SiMe_3)_2$ cleavage, a linear relationship is observed (Figure 6). This relationship shows that phosphine-sensitive trends in the protonolysis rate parallel those in chain-transfer rate (eq 20), further supporting the Scheme 2 scenario in which chain transfer is a protonolytic process.

Conclusions

This investigation demonstrates that phosphines act as efficient chain-transfer agents for Cp'_2Ln-mediated ethylene polymerizations. Moreover, the overall effectiveness of phosphine chain transfer in lanthanocene-mediated ethylene polymerizations decreases in the same order as the rate of $Ln-CH(SiMe_3)_2$ protonolysis:

$$H_2PPh \gg H_2PCy > HPPh_2 > HPEt_2 \approx HP^iBu_2 > HPCy_2$$

Primary phosphines are the most efficient chain-transfer agents, as evidenced by the fact that polymerizations conducted in the presence of cyclohexylphosphine and phenylphosphine produce only small quantities of low-molecular-weight cyclohexylphosphine-capped oligomers and ethylphenylphosphine, respectively. Organolanthanide-mediated hydrophosphination[17] and hydroamination[16,19] mechanistic observations suggest that intra- or intermolecular phosphine coordination stabilizes the Lewis acidic lanthanide center, likely favoring phosphine chain transfer and disfavoring ethylene insertion, in accord with the present results. Among secondary phosphines, diphenylphosphine is the most efficient chain-transfer agent as a consequence of both phosphine steric and electronic properties. Diethyl- and diisobutylphosphines are also found to be efficient chain-transfer agents for Cp'_2La-mediated polymerizations. Under the polymerization conditions studied, dicyclohexylphosphine is an ineffective chain-transfer agent for both Cp'_2La- and Cp'_2Y-mediated ethylene polymerizations, most likely a result of steric constraints. The efficiency of phosphine chain transfer increases with increasing lanthanide ionic radius, consistent with a sterically encumbered chain-transfer transition state.

A series of Cp'_2YPPh_2-mediated polymerizations with varying phosphine concentrations was conducted and revealed high polymerization rates, high product molecular weights, $M_w/M_n \approx 2.0$, negligible signatures of β-H elimination, 1:1 ratios of CH_3:phosphine chain termini, and a linear relationship between M_n and $[\text{diphenylphosphine}]^{-1}$—all consistent with a predominant protonolytic, phosphine chain-transfer mechanism. In addition, a linear relationship is observed between number average degree of polymerization and the rate of $Ln-CH(SiMe_3)_2$ protonolysis by the same phosphines. The ability to modify the resulting polymer characteristics by varying the phosphine substitution or lanthanide ion imbues the current system with considerable flexibility. Based on the analogies between organolanthanide-catalyzed hydrophosphination[17] and hydroamination[16,19] and the flexibility of the current system, the possibility of amine-capped polyethylenes remains promising. However, since the rates of Ln−C protonolysis are significantly more rapid with amines than with the corresponding phosphines ($\sim 10^4$ times),[17d] judicious choice of amine chain-transfer agent, catalyst, and polymerization conditions will be required.

We have shown here that lanthanocene-mediated hydrophosphination and ethylene polymerization can be coupled in a catalytic cycle to produce phosphine-terminated polyethylenes with high activities and narrow molecular weight distributions. Therefore, the addition of phosphines to organolanthanide-mediated ethylene polymerization systems is a versatile, efficient way of incorporating electron-rich functional groups into an otherwise inert polymer.

Acknowledgment. Financial support by the NSF (Grants Nos. CHE-0078998 and CHE-04157407) is gratefully acknowledged. We thank Dr. R. Lepointe of Dow Chemical, Dr. T. R. Jensen, and Dr. S. Schneider for helpful discussions. A.M.K thanks Ms. S. B. Amin for assistance with MALDI-TOF MS measurements.

Supporting Information Available: Figures S-1−S-3 as described in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

JA044174I