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Articles

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

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Amines of varying Brønsted acidity and steric encumberance are investigated as chain-transfer agents to functionalize polyolefins via organolanthanide-mediated olefin polymerization processes. Ethylene homopolymerizations are carried out with activated $Cp'_2LnCH(Si(CH_3)_3)_2$ ($Cp' = \eta^5$-Me_5C_5; Ln = La, Sm, Y, Lu) precatalysts in the presence of aniline, *n*-propylamine, *N*,*N*-bis(trimethylsilyl)amine, di-*sec*-butylamine, *N*-*tert*-butyl(trimethylsilyl)amine, di-isopropylamine, and dicyclohexylamine. In the presence of these amines, polymerization activities up to 10^4 g polymer/(mol of Ln•atm ethylene•h) and narrow product polymer polydispersities are observed, consistent with single-site polymerization processes. Amine chain-transfer efficiency follows the trend $C_6H_5NH_2 \approx {}^nC_3H_7NH_2 << [Si(CH_3)_3]_2NH \approx {}^{sec}Bu_2NH <$ N-${}^tBu[Si(CH_3)_3]NH \approx {}^iPr_2NH < Cy_2NH$ to yield polyethylenes of the structure $H(CH_2CH_2)_nNRR'$, where an efficient chain-transfer agent is defined as a reagent that both terminates polymer chain growth and facilitates reinitiation of polymer chain growth. Under the conditions investigated, primary amines are found to be the most inert toward Cp'_2La-mediated polymerizations, affording no detectable insertion products, while di-*sec*-butylamine and *N*,*N*-bis(trimethylsilyl)amine are marginally efficient and produce monoethylene insertion products. In contrast, *N*-*tert*-butyl(trimethylsilyl)amine and di-isopropylamine afford amine-capped oligoethylenes, while dicyclohexylamine is the most efficient chain-transfer agent investigated, producing high molecular weight amine-terminated polyethylenes. For these Ln catalysts, dicyclohexylamine chain transfer exhibits a linear relationship between product M_n and [dicyclohexylamine]$^{-1}$, consistent with a well-behaved aminolysis chain termination pathway. In all of the above systems, protonolysis appears to be the dominant chain-transfer pathway. Organotitanium-mediated ethylene and propylene polymerizations in the presence of secondary amines result in modest polymerization rates with activities of 10^4 g polymer/(mol of Ti•atm ethylene•h).

Introduction

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

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(1) Recent reviews of single-site olefin polymerization and copolymerization: (a) Marks, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 15288–15354, and contributions therein (special feature on "Polymerization"). (b) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (c) Pedeutour, J.-N.; Radhakrishnan, K.; Cramail, H.; Deffieux, A. *Macromol. Rapid Commun.* **2001**, *22*, 1095. (d) Chen, Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (e) Gladysz, J. A. *Chem. Rev* **2000**, *100*, special issue on "Frontiers in METAL-CATALYZED Polymerization". (f) Marks, T. J., Stevens, J. C., Eds. *Top. Catal*. **1999**, *7*, andreferences therein. (g) Jordan, R. F., Ed. *J. Mol. Catal*. **1998**, *128*, andreferences therein. (h) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 144–187. (i) Bochmann, M. J. *J. Chem. Soc., Dalton Trans.* **1996**, 255–270, and references therein. (j) Brintzinger, H.-H.; Fisher, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143–1170. (k) Simonazzi, T.; Nicola, A.; Aglietto, M.; Ruggeri, G. In *Comprehensive Polymer Science*; Allen, G., Aggarwal, S. L., Russo, S., Eds.; Pergamon Press: Oxford, 1992; First Supplement, Chapter 7.

(2) Effects of functional groups and branching on polyolefin properties: (a) Chung, T. C. *Prog. Polym. Sci.* **2002**, *27*, 39. (b) Imuta, J.-I.; Kashiwa, N.; Toda, Y. *J. Am. Chem. Soc.* **2002**, *124*, 1176. (c) Dong, J. Y.; Wang, Z.; Hong, H.; Chung, T. C. *Macromolecules* **2002**, *35*, 9352. (d) Chung, T. C. *Polym. Mater. Sci. Eng.* **2001**, *84*, 33. (e) Chum, P. S.; Kruper, W. J.; Guest, M. J. *Adv. Mater.* **2000**, *12*, 1759. (f) Alt, H. G.; Föttinger, K.; Milius, W. J. *Organomet. Chem.* **1999**, *572*, 21. (g) Harrison, D.; Coulter, I. M.; Wang, S. T.; Nistala, S.; Kuntz, B. A.; Pigeon, M.; Tian, J.; Collins, S. *J. Mol. Catal. A: Chem.* **1998**, *128*, 65. (h) Nesarikar, A. R.; Carr, S. H.; Khait, K.; Mirabella, F. M. *J. Appl. Polym. Sci.* **1997**, *63*, 1179.

(3) Reviews on post-polymerization modification: (a) Boaen, N. K.; Hillmyer, M. A. *Chem. Soc. Rev* **2005**, *34*, 267. (b) Mülhaupt, R. *Macromol. Chem. Phys.* **2003**, *204*, 289.

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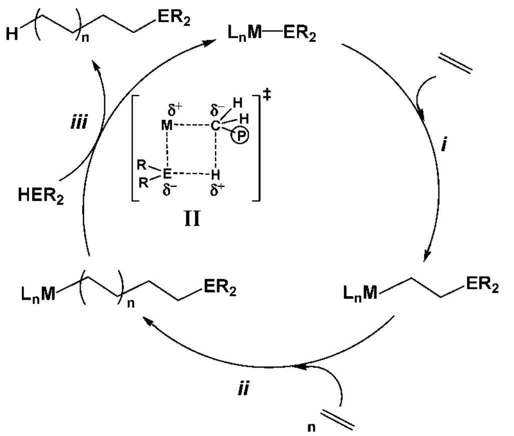
reagent-tolerant late transition metal catalysts, which have modest polymerization activities.

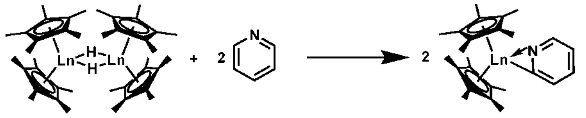
An alternative, versatile approach to polyolefin functionalization involves implementation of chain-transfer processes and agents, with the latter defined as chemical reagents that both terminate and facilitate the reinitiation of polyolefin chain growth and can efficiently control molecular weight while simultaneously and selectively introducing heteroatom functionality into the macromolecular architecture. To date, electron-deficient/neutral chain-transfer agents such as alanes, boranes, and silanes have been successfully introduced into catalytic single-site olefin polymerization processes. In contrast to the pathways outlined above, functionally analogous processes with electron-rich chain-transfer agents have been extensively characterized only for phosphines.[8] Here, the catalytic cycle is envisioned to proceed via sequences of (i) insertion of C−C unsaturation into the metal−heteroatom bond, (ii) multiple insertions of C−C unsaturation into the resulting M−C bond(s), and (iii) protonolysis of the metal–polymeryl bond, presumably via a polar four-center σ-bond metathesis transition state, to release the functionalized polyolefin and regenerate the active catalyst (Scheme 1). While the synthesis of phosphine-terminated polyethylenes can be achieved via this route, the product polymers are generally of specialized interest. In contrast, amine-terminated polyolefins, if accessible via chain-transfer routes, have broad established utility in a variety of applications including, but not limited to, drug and gene delivery, antibacterial treatments, sensors, adhesives, and ion-exchange resins.[12]

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

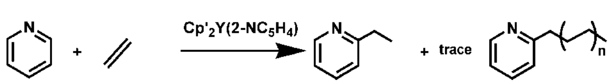


Ⓟ = Polymer chain; E = P, N; R = alkyl, aryl

Organolanthanide complexes[13] are versatile catalysts for homogeneous single-site coordinative α-olefin polymerization.[1] Thus, $[\mathrm{Cp'_2LnH}]_2$[14] ($\mathrm{Cp'} = \eta^5\text{-}\mathrm{Me_5C_5}$) and $[\mathrm{Me_2\text{-}SiCp''_2LnH}]_2$[15] ($\mathrm{Cp''} = \eta^5\text{-}\mathrm{Me_4C_5}$) catalysts efficiently polymerize ethylene to high molecular weight polyethylene with turnover frequencies exceeding 1800 s^{-1} and with narrow product polydispersities. Furthermore, both primary and secondary organosilanes function as efficient chain-transfer agents for organolanthanide-catalyzed olefin homopolymerizations and ethylene/α-olefin copolymerizations (via a mechanism coupling Ln−H insertion and Ln−C/Si−H transposition)[5] to yield silane-functionalized polyolefins. $\mathrm{Cp'_2Y}$(2-pyridyl), synthesized from $[\mathrm{Cp'_2YH}]_2$ via aryl C−H activation (eq 1),[16] also mediates chain transfer to afford 2-ethylpyridine and traces of polymeric products in the presence of excess ethylene and pyridine (eq 2).[16]



(1)



(2)

Recently, organolanthanide complexes have been used to selectively synthesize phosphine-capped polyethylenes with activities as high as 10^7 g polymer/(mol Ln·atm·h) as noted above. A diverse range of secondary phosphines effects selec-

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(4) Copolymerization with polar comonomers: (a) Zhang, X.; Chen, S.; Li, H.; Zhang, Z.; Lu, Y.; Wu, C.; Hu, Y. *J. Polym. Sci: Part A: Polym Chem.* **2007**, *45*, 59. (b) Williams, B. S.; Leatherman, M. D.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2005**, *127*, 5132. (c) Liu, W.; Malinoski, J. M.; Brookhart, M. *Organometallics* **2002**, *21*, 2836. (d) Shultz, C. S.; DeSimone, J. M.; Brookhart, M. *Organometallics* **2001**, *20*, 16. (e) Tempel, D. J.; Johnson, L. K.; Huff, R. L.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6686. (f) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (g) Shultz, C. S.; Ledford, J.; DeSimone, J. M.; Brookhart, M. *J. Am. Chem. Soc.* **2000**, *122*, 6351.

(5) Silane chain transfer agents: (a) Amin, S. B.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 2938. (b) Amin, S. B.; Marks, T. J. *Organometallics* **2007**, *26*, 2960. (c) Amin, S. B.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 4506. (d) Makio, H.; Koo, K.; Marks, T. J. *Macromolecules* **2001**, *34*, 4676. (e) Koo, K.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 8791. (f) Koo, K.; Fu, P.-F.; Marks, T. J. *Macromolecules* **1999**, *32*, 981. (g) Koo, K.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 4019. (h) Fu, P.-F.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 10747.

(6) Borane chain transfer agents: (a) Lu, Y.; Hu, Y.; Wang, Z. M.; Manias, E.; Chung, T. C. *J. Polym. Sci.: Part A: Polym. Chem.* **2002**, *40*, 3416. (b) Chung, T. C.; Xu, G.; Lu, Y.; Hu, Y. *Macromolecules* **2001**, *34*, 8040. (c) Xu, G.; Chung, T. C. *Macromolecules* **1999**, *32*, 8689. (d) Xu, G.; Chung, T. C. *J. Am. Chem. Soc.* **1999**, *121*, 6763.

(7) Metallocene-mediated alane chain transfer in propylene polymerization systems see: (a) Tynys, A.; Eilertsen, J. L.; Rytter, E. *Macromol. Chem. Phys.* **2006**, *207*, 295. (b) Quintanilla, E.; di Lena, F.; Chen, P. *Chem. Commun.* **2006**, 4309. (c) Fan, G.; Dong, J.-Y. *J. Mol. Catal. A: Chem.* **2005**, *236*, 246. (d) Kukral, J.; Lehmus, P.; Klinga, M.; Leskela, M.; Rieger, B. *Eur. J. Inorg. Chem.* **2002**, 1349. (e) Gotz, C.; Rau, A.; Luft, G. *Macromol. Mater. Eng.* **2002**, *287*, 16. (f) Liu, J.; Stovneng, J. A.; Rytter, E. *J. Polym. Sci; Part A: Polym. Chem.* **2001**, *39*, 3566.

(8) Phosphine chain-transfer agents: (a) Kawaoka, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 6311. (b) Kawaoka, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 12764.

(9) Amine chain transfer agents: Amin, S. B.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 10102.

(10) Thiophene chain transfer: Ringelberg, S. N.; Meetsma, A.; Hessen, B.; Teuben, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 6082.

(11) Organozinc chain transfer: (a) Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science* **2006**, *312*, 714. (b) van Meurs, M.; Britovsek, G. J. P.; Gibson, V. C.; Cohen, S. A. *J. Am. Chem. Soc.* **2005**, *127*, 9913, and references therein.

(12) Applications of amine-functionalized polymers: (a) Ji, H.; Sakellariou, G.; Mays, J. W. *Macromolecules* **2007**, *40*, 3461. (b) Yang, Y.; Sheares, V. V. *Polymer* **2007**, *48*, 105. (c) Yang, Y.; Lee, J.; Cho, M.; Sheares, V. V. *Macromolecules* **2006**, *39*, 8625. (d) Dizman, B.; Elasri, M. O.; Mathias, L. J. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 5965.

(13) For recent reviews of organolanthanide-mediated olefin polymerization see: (a) Gromada, J.; Carpentier, J.-F.; Mortreux, A. *Coord. Chem. Rev.* **2004**, *248*, 397. (b) Hou, Z.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, *231*, 1. (c) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193.

(14) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

(15) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103.

(16) Deelman, B.-J.; Stevels, W. M.; Teuben, J. H.; Lakin, M. T.; Spek, A. L. *Organometallics* **1994**, *13*, 3881.

(17) Hydrophosphination: (a) Kawaoka, A. M.; Douglass, M. R.; Marks, T. J. *Organometallics* **2003**, *22*, 4030. (b) Douglass, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10221. (c) Douglass, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 1824.

tive, catalytic C−P bond formation and chain termination, including diphenyl-, diethyl-, and di-isobutylphosphine. Primary phosphines (e.g., cyclohexylphosphine) are also efficient chain-transfer agents, producing phosphine-capped oligoethylenes. These results demonstrate the ability of electron-rich chain-transfer agents to selectively and catalytically functionalize polyolefin chains. On the basis of analogies between hydrophosphination[17] and hydroamination,[18] amine chain-transfer processes would seem to be viable in single-site organolanthanide-mediated olefin polymerization catalysis. However, since Ln−C protonolyses by amines are established to be $\sim 10^4$ times faster than by the corresponding phosphines,[18b] careful tuning of the amine chain-transfer agent's steric and electronic characteristics is essential for achieving efficient chain propagation (Scheme 1, rate (*i, ii*) ≫ rate (*iii*)).

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

Experimental Section

Materials and Methods. All manipulations of air-sensitive materials were carried out with rigorous exclusion of oxygen and moisture in flame- or oven-dried Schlenk-type glassware on a dual-manifold Schlenk line, or interfaced to a high-vacuum line (10^{-6} Torr), or in a N_2-filled MBraun glovebox with a high-capacity recirculator (<1 ppm of O_2; <1 ppm of H_2O). Argon, hydrogen, and ethylene (Airgas, prepurified) were purified by passage through MnO oxygen-removal and Davison 4 A molecular sieve columns. Hydrocarbon solvents (*n*-pentane and toluene) were dried using activated alumina columns according to the method described by Grubbs[19] and were additionally vacuum-transferred from Na/K alloy immediately prior to vacuum line manipulations. All NMR solvents were purchased from Cambridge Isotope Laboratories, stored under argon and over Na/K alloy in vacuum-tight storage flasks, and distilled immediately prior to use. All organic starting materials were purchased from Aldrich Chemical Co. and were used without further purification unless otherwise stated. Dicyclohexylamine was dried with $LiAlH_4$ for 48 h, transferred onto molecular sieves 3 times, and stored in a vacuum-tight storage flask. All other amine substrates (*N,N*-bis(trimethylsilyl)amine, *N-tert*-butyl(trimethylsilyl)amine, di-isopropylamine, di-*sec*-butylamine, and aniline) were dried over CaH_2 for a minimum of 5 days, distilled onto molecular sieves 2 times, and stored in vacuum-tight storage flasks. The monomer 1-hexene was stirred over CaH_2 for 5 days and distilled immediately prior to use. The organolanthanide precatalysts $Cp'_2LnCH(SiMe_3)_2$ (Ln = La, Sm, Y, Lu) were synthesized according to a published procedure.[15] The organotitanium precatalyst $Me_2Si(Me_4C_5)(N^tBu)TiMe_2$[20] and cocatalyst $Ph_3C^+B(C_6F_5)_4^-$[21] were prepared by published procedures.

Physical and Analytical Measurements. NMR spectra were recorded on either an Inova-400 (400 MHz ^1H; 100 MHz ^{13}C) or Inova-500 (500 MHz ^1H; 125 MHz ^{13}C) instrument. For polymer NMR characterization, 50–75 mg samples were dissolved in 0.5–0.7 mL of $C_2D_2Cl_4$ in a 5 mL NMR tube by heating the mixture in a 120 °C oil bath. Melting temperatures of polymers were measured by DSC (DSC 2920, TA Instruments, Inc.) from the second scan with a heating rate of 20 °C/min. GPC analyses of polymer samples were performed on a Polymer Laboratories PL-GPC 220 instrument using three PLgel 10 μm mixed columns; operation temperature, 150 °C; mobile phase, 1,2,4-trichlorobenzene (stabilized with 125 ppm BHT); flow rate, 1 mL/min). GC-MS analyses were performed on a HP 6890 instrument equipped with a Zebron ZB-5 dimethylpolysiloxane column (30 m × 250 μm × 0.25 μm) interfaced to a HP 6890 mass-selective detector using *n*-propylamine as an internal standard. MALDI-TOF MS spectra were collected on a PE Biosystems Voyager System 6050 time-of-flight mass spectrometer using a nitrogen laser for MALDI ($\lambda = 337$ nm). The measurements were performed in the reflector mode. Dithranol was used as the matrix with a polymer concentration of ~10 mg/mL and a polymer:matrix ratio of ~1:1 by mass. Melting points were measured on a Büchi B-450 melting point apparatus and are uncorrected. Elemental analyses were performed by Midwest Microlabs, Indianapolis, IN.

Organolanthanide-Mediated Polymerization of Ethylene in the Presence of Dicyclohexylamine. Representative Experiment. In the glovebox, a three-necked Morton flask, which had been dried overnight at 160 °C, equipped with a large stir bar and thermocouple (Omega type K stainless steel sheathed), was charged with dry toluene (30 mL). The flask was next attached to a high-vacuum line and the toluene was freeze–thaw degassed, followed by introduction of ethylene (1.0 atm) with rapid stirring. In the glovebox, $Cp'_2LaCH(SiMe_3)_2$ (0.010 mmol) was placed in a dry storage tube (dried overnight at 160 °C) equipped with a stir bar and 4 mL of dry toluene. The catalyst storage tube was attached to the high-vacuum line, and next, dicyclohexylamine (0.20 mL) was injected into the storage tube with rapid stirring. The solution was stirred for several min, after which time the contents were taken up in an N_2-purged syringe. The catalyst solution was next injected through the septum-sealed polymerization flask sidearm into the rapidly stirring reaction flask. After 90 min, methanol (10 mL) was injected to quench the reaction. Excess methanol (~500 mL) was then used to precipitate the polymer. The product polymer (0.50 g) was collected by filtration, washed with methanol (200 mL), and dried *in vacuo* at 80 °C for 48 h. $T_m = 138$ °C. ^1H NMR (400 MHz, $C_2D_2Cl_4$): δ 0.98 ($-CH_3$), 1.2–1.6 ($-CH_2-$), 2.4 ($-CH_2N-$ and $-CHN-$). ^{13}C NMR (100 MHz, $C_2D_2Cl_4$): δ 15.7, 24.1, 27.8, 29.1, 30.8, 51.7, 61.

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(18) For recent studies on organolanthanide-catalyzed hydroamination see: Yu, X.; Marks, T. J. *Organometallics* **2007**, *26*, 365. (b) Rastaetter, M.; Zulys, A.; Roesky, P. W. *Chem.−Eur. J.* **2007**, *13*, 3606. (c) Motta, A.; Fragala, I. L.; Marks, T. J. *Organometallics* **2006**, *25*, 4763. (d) Zhao, J.; Marks, T. J. *Organometallics* **2006**, *25*, 4763. (e) Tobisch, S. *Chem.−Eur. J.* **2006**, *12*, 2520. (f) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. *J. Am. Chem. Soc.* **2006**, *128*, 3748. (g) Reigert, D.; Collin, J.; Meddour, A.; Schulz, E.; Trifonov, A. *J. Org. Chem.* **2006**, *71*, 2514. (h) Panda, T. K.; Zulys, A.; Gamer, M. T.; Roesky, P. W. *J. Organomet. Chem.* **2005**, *690*, 5078. (i) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673. (j) Ryu, J.-S.; Marks, T. J. *J. Org. Chem.* **2004**, *69*, 1038. (k) Seyam, A. M.; Stubbert, B. D.; Jensen, T. R.; O'Donnell, J. J., III; Stern, C. L.; Marks, T. J. *Inorg. Chim. Acta* **2004**, *357*, 4029. (l) Hong, S.; Kawaoka, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 15878. (m) Molander, G. A.; Pack, S. K. *Tetrahedron* **2003**, *59*, 10581.

(19) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

(20) (a) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. European Patent Applications EP416815A2, 1991. (b) Devore, D. European Patent Application EP514828A1, 1992.

(21) Ihara, E.; Young, V. G.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 8277–8278.

Organolanthanide-Mediated Polymerization of Ethylene in the Presence of Di-isopropylamine. Representative Experiment. The same procedure as for the above reaction was employed except that di-isopropylamine was used as the chain-transfer agent, and a 5.0 mL aliquot of the reaction mixture was reserved for analysis. Under high-vacuum conditions (10^{-6} Torr), the volatile portion of the 5.0 mL aliquot was vacuum-transferred away from the nonvolatile portion (0.06 g). The volatile solution was analyzed by GC-MS, and the nonvolatile portion was analyzed by MALDI-TOF MS. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 0.88 ($-CH_3$), 1.25 ($-CH_3$), 1.4–1.8 ($-CH_2-$), 2.0 ($-CH_2N-$), 2.35 ($-CH-$); the products $H(CH_2CH_2)_nN(^iPr)_2$, $n = 10$–17 and $n = 1$, were detected by MALDI-TOF and GC-MS, respectively.

Organolanthanide-Mediated Polymerization of Ethylene in the Presence of Di-*sec*-butylamine. Representative Experiment. The same procedure as for the above reaction was employed, except that di-*sec*-butylamine was used as the chain-transfer agent. The products $H(CH_2CH_2)_nN[C_2H_5CH(CH_3)]_2$, $n = 1, 2$, were detected by GC-MS in a ~40% yield.

Organolanthanide-Mediated Polymerization of Ethylene in the Presence of *N,N*-Bis(trimethylsilyl)amine. Representative Experiment. The same procedure as for the above reaction was employed, except for that *N,N*-bis(trimethylsilyl)amine was used as the chain-transfer agent. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 0.16 ($-SiMe_3$), 0.94 ($-CH_3$), 1.2–1.6 ($-CH_2-$), 2.1 ($-CH_2N-$), 2.4 ($-CHN$); the products $H(CH_2CH_2)_nN(SiMe_3)_2$, $n = 1, 2$, were detected by GC-MS in a ~30% yield.

Organolanthanide-Mediated Polymerization of Ethylene in the Presence of *N-tert*-Butyl(trimethylsilyl)amine. Representative Experiment. The same procedure as for the above reaction was employed, except that *N-tert*-butyl(trimethylsilyl)amine was used as the chain-transfer agent. The products $H(CH_2CH_2)_nN^tBu(SiMe_3)$ (0.04 g), $n = 6$–8 and $n = 1$, were detected by MALDI-TOF and GC-MS, respectively.

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

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

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

NMR-Scale Organolanthanide-Mediated Polymerization of Ethylene in the Presence of *n*-Propylamine. Representative Experiment. In the glovebox, an NMR tube equipped with a Teflon valve was loaded with $Cp'_2LaCH(SiMe_3)_2$ (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 *n*-propylamine (0.06 mL, 0.73 mmol) and C_6D_6 (0.2 mL) were added via syringe under an argon flush. The tube was evacuated and back-filled with Ar while frozen at –78 °C, and then the tube was sealed. The sample tube was warmed quickly, and 1.0 atm of ethylene was bubbled through the solution for 30 min. The polymerization reaction was monitored by ^{1}H NMR spectroscopy.

Synthesis of *N*-Cyclohexyl-*N*-octadecylcyclohexanamine. A solution of dicyclohexylamine (657 μl, 3.3 mmol) in dry CH_2Cl_2 was added to a stirred solution of stearoyl chloride (1 g, 3.3 mmol) and triethylamine (1.38 mL, 9.9 mmol). The reaction mixture was stirred at room temperature overnight under N_2 and then poured into 1 N HCl solution. The mixture was extracted with CH_2Cl_2 (3 times), and the combined organic layers were washed with 1 N NaOH, water, and brine and then dried over Na_2SO_4. This crude product was used without further purification for the next step. To a stirred suspension of $LiAlH_4$ (60 mg, 1.6 mmol) in Et_2O at 0 °C under N_2 was slowly added a solution of the above amide (470 mg, 1.05 mmol) in Et_2O. The reaction mixture was allowed to warm to room temperature and stirred under reflux for 2 h. Next, the mixture was diluted with Et_2O and then carefully quenched by sequential additions of water, 15% aqueous NaOH, and water. Stirring at room temperature for a further 30 min yielded a colorless solution with a white precipitate, which was then removed by filtration through a Celite pad. The filtrate was then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude amine was purified by column chromatography (silica gel, hexane/EtOAc = 20:1) to afford 330 mg (0.76 mmol, 72% isolated yield) of pure amine as a white solid; mp 33.7–34.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.49 (m, 2 H), 2.41 (t, 2 H), 1.70 (m, 10 H), 1.55 (d, 3 H), 1.35–1.13 (m, 36 H), 1.04 (m, 3 H), 0.85 (t, 3 H). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 2.50 (br s, 4 H), 1.75 (m, 10 H), 1.60 (d, 3 H), 1.39–1.07 (m, 39 H), 0.89 (t, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 58.3, 46.90, 32.14, 31.78, 29.91, 29.88, 29.58, 27.66, 26.65, 26.57, 22.91, 14.34. ^{13}C NMR (100 MHz, $C_2D_2Cl_4$): δ 60.7, 47.71, 31.80, 29.60, 29.25, 29.02, 27.17, 25.40, 22.60, 14.12. Anal. Calcd for $C_{30}H_{59}N$: C, 83.06; H, 13.71; N, 3.23. Found: C, 82.96; H, 13.73; N, 3.31.

Organotitanium-Mediated Polymerization of Ethylene in the Presence of Dicyclohexylamine. Representative Experiment. In the glovebox, a three-necked Morton flask, which had been dried overnight at 160 °C, equipped with a large stir bar and thermocouple, was charged with dry toluene (30 mL). The flask was next attached to a high-vacuum line and the toluene was freeze–thaw−degassed, followed by introduction of ethylene (1.0 atm) with rapid stirring. Next, dicyclohexylamine (0.25 mL) was rapidly injected into the flask under argon flush and with rapid stirring. In the glovebox, a 5.0 mL sample vial equipped with a septum cap was charged with 3.20 mg (0.010 mmol) of $Me_2Si(Me_4C_5)(N^tBu)TiMe_2$ (CGCTiMe$_2$) and 9.22 mg (0.010 mmol) of $Ph_3C^+B(C_6F_5)_4^-$. A measured amount of toluene (4.0 mL) was then syringed into the vial with a dry, N_2-purged gas-tight syringe. The vial was shaken for several minutes, and the contents were taken up in the syringe and then removed from the glovebox immediately prior to the polymerization experiment. The catalyst solution was next rapidly syringed through the septum-sealed polymerization flask sidearm into the rapidly stirring reaction flask. After 120 min, methanol (10 mL) was injected to quench the reaction. Excess methanol (~500 mL) was then used to precipitate the polymer. The product polymer (0.040 g) was collected by filtration, washed with methanol (200 mL), and dried *in vacuo* at 80 °C for 48 h. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 0.98 ($-CH_2$-, $-CH_3$), 1.2–1.6 (cyclohexyl $-CH_2-$), 2.4 ($-CH_2N-$ and $-CHN-$). ^{13}C NMR (100 MHz, $C_2D_2Cl_4$): δ 24.6 (cyclohexyl $-CH_2-$), 29.3 ($-CH_2-$), 54.3 ($-CH_2N-$).

Organotitanium-Mediated Polymerization of Propylene in the Presence of Dicyclohexylamine. Representative Experiment. The same procedure as for the above reaction was employed, except that 1.0 atm of propylene pressure was used as the monomer. The product polymer (0.20 g) was collected as described above. ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): δ 0.95 ($-CH_3$), 1.1–1.3 ($-CH_2-$), 1.3 (cyclohexyl $-CH_2-$), 1.7 ($-CH-$), 2.4 ($-CH_2N-$), 3.5 ($-CHN-$). ^{13}C NMR (100 MHz, $C_2D_2Cl_4$): δ 21 ($-CH_3-$), 29 ($-CH_2-$), 48 ($-CH-$), 56 ($-CH_2N-$).

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

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

entry	precatalyst[a]	[precat.] (μM)	[$(C_6H_{11})_2NH$] (mM)	activity[b] ($\times 10^4$)	M_n[c] ($\times 10^3$)	M_w/M_n[c]	T[d]	T_m[e] (°C)
1	Cp'_2LuR	370	34	<0.01[f]			24	
2	Cp'_2YR	330	34	0.01[f]			24	
3	Cp'_2SmR	330	34	0.70	260	2.7	24	138
4	Cp'_2LaR	360	34	1.00	200	2.5	24	138
5	Cp'_2LaNCy_2	330	8.4	2.50	1100	2.0	24	139
6	Cp'_2LaNCy_2	290	20	2.03	270	2.1	24	138
7	Cp'_2LaNCy_2	350	42	0.91	130	1.7	25	139
8	Cp'_2LaNCy_2	360	84	0.20	91	1.6	25	137
9	Cp'_2LaNCy_2	360	126	0.10	53	2.1	24	138

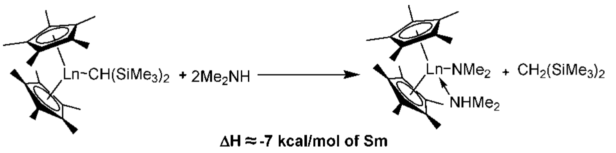
[a] $Cp' = Me_5C_5$; polymerization conditions: 30 mL of toluene, 90 min. [b] Units = g/(mol Ln·atm ethylene·h. [c] By GPC in 1,2,4-trichlorobenzene vs polyethylene standards. [d] Reaction temperature. [e] By DSC. [f] Trace yields of polymer obtained (<10 mg). Cy = cyclohexyl; R = $CH(TMS)_2$ or secondary amine.

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

Results

The goal of this research was to investigate the applicability, scope, and reaction mechanism of amines as electron-rich, C−N bond-forming chain-transfer agents in single-site olefin polymerization. Here we extend our earlier, preliminary study[9] to include other amines in organolanthanide-mediated polymerization systems. After a brief discussion of the catalyst activation process, we discuss the efficacy of dicyclohexyl-, di-isopropyl-, di-*sec*-butyl-, *N*-*tert*-butyl(trimethylsilyl)-, *N*,*N*-bis(trimethylsilyl)amine, aniline, and *n*-propylamine as chain-transfer agents. Next, the effect of amine and lanthanide ion on polymerization characteristics will be discussed from a mechanistic standpoint. Small molecule hydroamination phenomenology will be used to understand and place in context the present observations and trends.

Organolanthanide Catalyst Activation. The chain termination step of the proposed catalytic cycle (Scheme 1, step *iii*) involves Ln−C σ-bond protonolysis with concomitant formation of a lanthanide amido complex (or amine-amido complex, depending on the amine).[18] This step is thermodynamically favorable, as evidenced by calorimetrically characterized eq 3.[22a] Ln−C (σ) aminolysis is very rapid for $Cp'_2LnCH(SiMe_3)_2$ complexes at room temperature and proceeds at rates up to 10^4 times those of the analogous phosphine reagents.[18b] Since Cp'_2Ln-amido precatalyst formation is essentially instantaneous at room temperature, they are conveniently generated *in situ* from the corresponding hydrocarbyls under typical catalytic conditions.



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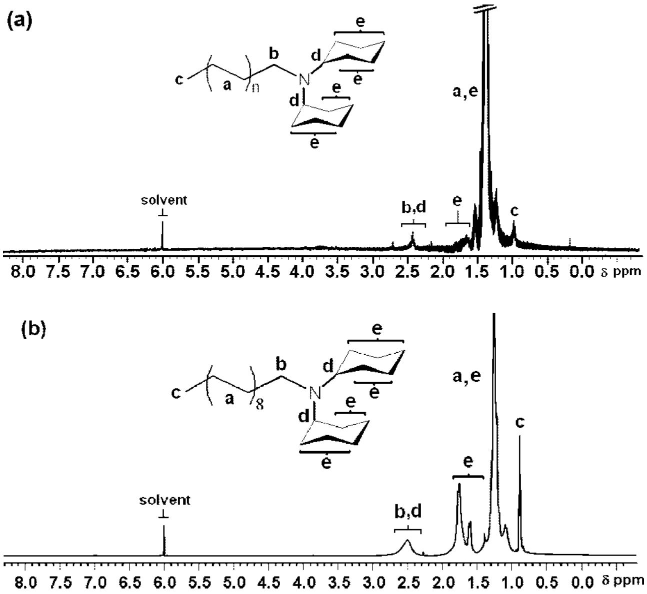

Figure 1. ^{1}H NMR spectra of (a) a dicyclohexylamine-capped polyethylene (M_n = 131 600) produced by Cp'_2La-mediated polymerization (400 MHz, $C_2D_2Cl_4$, 130 °C) and (b) *N*-cyclohexyl-*N*-octadecylcyclohexanamine model compound (400 MHz, $C_2D_2Cl_4$, 21 °C).

Chain-Transfer Efficiency of Dicyclohexylamine in Organolanthanide-Mediated Ethylene Polymerizations. Dicyclohexylamine was investigated as a chain-transfer agent for organolanthanide-mediated ethylene polymerizations (Table 1). All polymerizations were carried out under 1.0 atm of ethylene pressure using rigorously anaerobic/anhydrous conditions and procedures minimizing mass transport effects with $Cp'_2LnCH(SiMe_3)_2$ precatalysts,[15] and with olefin concentrations maintained in pseudo-zero-order excess. Since polymers would be produced via ethylene insertion into the Ln−N bond, and the amine moiety is transferred to the polymer chain at the beginning of chain growth, Cp'_2LnNCy_2 ($Cp' = \eta^5$-Me_5C_5; Cy = cyclohexyl) complexes were first generated prior to polymerization. The colorless precatalyst solution remains colorless upon addition of amine chain-transfer agent and throughout the course of the polymerization reaction. ^{1}H NMR spectra of the product amine-terminated polyethylenes produced using *in situ*-generated Cp'_2LaNCy_2 (Cy = cyclohexyl) exhibit merged $-CH_2N$, $-CHN$ amine (δ 2.41), $-CH_2-$ polyethylene backbone (δ 1.2–1.5), and $-CH_3$ chain end (δ 0.98) resonances (Figure 1a), while ^{13}C NMR spectra likewise exhibit characteristic amine (δ 51) and polyethylene backbone (δ 29 and 24) resonances (Figure 2a). Furthermore, the absence of vinylic resonances in the ^{1}H and ^{13}C NMR spectra argues that chain

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[22] (a) Nolan, S. P.; Stern, D.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7844. (b) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.

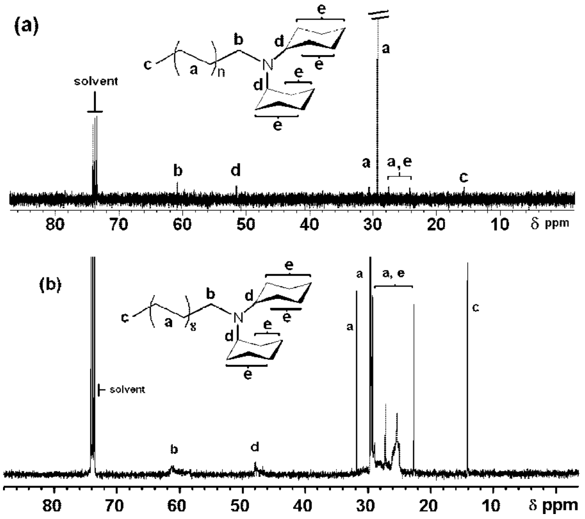


Figure 2. ^{13}C NMR spectra of (a) a dicyclohexylamine-capped polyethylene (M_n = 131,600) produced by Cp′$_2$La-mediated ethylene polymerization in the presence of dicyclohexylamine (100 MHz, $C_2D_2Cl_4$, 130 °C) and (b) *N*-cyclohexyl-*N*-octadecylcyclohexanamine model compound (100 MHz, $C_2D_2Cl_4$, 21 °C).

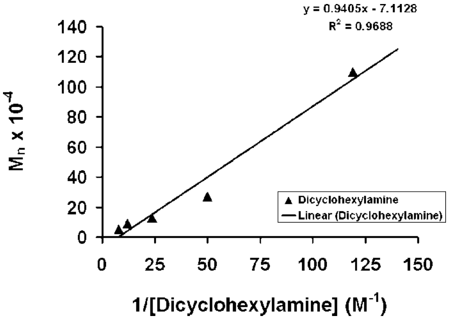


Figure 3. Relationship of polyethylene number average molecular weight (GPC versus polyethylene) to inverse $(C_6H_{11})_2NH$ concentration at fixed catalyst and ethylene concentrations. Several intermediate M_n samples formed gels and could not be analyzed by GPC.

termination via β-hydride elimination is insignificant, while the ~1: 1 –CH_2N:–CH_3 ^{1}H NMR chain end resonance ratio argues that one amine functional group is delivered to the terminus of each polyethylene chain. ^{1}H and ^{13}C NMR spectra of the model compound *N*-cyclohexyl-*N*-octadecylcyclohexanamine (Figures 1b and 2b, respectively) are in good agreement with the polymer spectral structural assignments. Furthermore, the resulting amine-capped polyethylenes have narrow, monomodal polydispersities, consistent with a single-site process (Table 1; see more below).

For polymerizations conducted in the presence of constant [dicyclohexylamine], lanthanide ionic radius and polymer molecular weight appear to be inversely related. Ethylene polymerizations mediated by *in situ*-generated Cp′$_2$LaNCy$_2$ in the presence of dicyclohexylamine (~34 mM) require relatively long reaction times to produce significant amounts of polymer with slightly lower molecular weight (M_n = 200 000; Table 1, entry 4) versus the polyethylenes produced by Cp′$_2$SmNCy$_2$ (M_n = 260 000; Table 1, entry 3).

Furthermore, at constant Cp′$_2$LaNCy$_2$ and ethylene concentrations, product polyethylene molecular weight is inversely proportional to [amine] (Table 1, entries 5–9, Figure 3), supporting the mechanism shown in Scheme 1. Dicyclohexylamine was also investigated as a chain-transfer agent in propylene and 1-hexene homopolymerization systems using Cp′$_2$LaCH(SiMe$_3$)$_2$ as the precatalyst. MALDI-TOF and GC-MS analyses of both quenched polymerization mixtures indicate no significant quantities of α-olefin insertion products. Additional mechanistic insights are presented in the Discussion section.

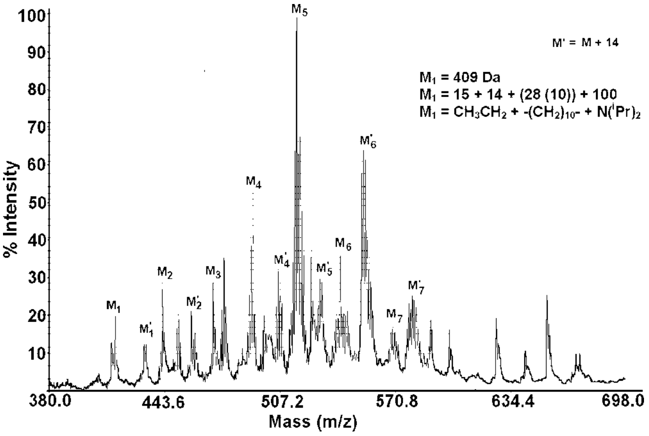


Figure 4. MALDI-TOF mass spectrum of a di-isopropylamine-capped oligoethylene produced by Cp′$_2$La-mediated ethylene polymerization in the presence of di-isopropylamine.

Chain-Transfer Efficiency of Di-isopropylamine. Di-isopropylamine was also investigated as a chain-transfer agent for ethylene polymerization using a Cp′$_2$LaCH(SiMe$_3$)$_2$ precatalyst. *In situ*-generated Cp′$_2$LaN^{i}Pr$_2$ is colorless, similar to Cp′$_2$LaCH(SiMe$_3$)$_2$, and during the course of the polymerization the reaction solution remains colorless. The concentration of vinyl chain end resonances in the product polymer ^{1}H NMR spectrum is below the detection limits, again indicating that chain termination via β-hydride elimination is negligible and that di-isopropylamine chain transfer is the dominant chain-transfer pathway (Figure S1). Furthermore, MALDI-TOF analysis of the product oligoethylenes indicates 10–17 ethylene insertions per di-isopropylamine chain end (Figure 4). GC-MS analysis of the volatile portion reveals trace monoethylene insertion product.

Chain-Transfer Efficiency of *N*-*tert*-Butyl(trimethylsilyl)-amine. N-*tert*-butyl(trimethylsilyl)amine was also investigated as a chain-transfer agent using Cp′$_2$LaCH(SiMe$_3$)$_2$ as the precatalyst. *In situ*-generated Cp′$_2$LaN(^{t}Bu)(SiMe$_3$) is colorless, similar to Cp′$_2$LaCH(SiMe$_3$)$_2$, and the reaction solution remains colorless during the course of the polymerization. The MALDI-TOF analyses of the product oligomeric material indicate 6–8 ethylene insertions per *N*-*tert*-butyl(trimethylsilyl)amine chain end (Figure 5). GC-MS analysis of the volatile portion reveals trace monoethylene insertion product.

Chain-Transfer Efficiency of Di-*sec*-butylamine and *N*,*N*-Bis(trimethylsilyl)amine. Di-*sec*-butylamine and *N*,*N*-bis(trimethylsilyl)amine were also investigated as chain-transfer agents using Cp′$_2$LaCH(SiMe$_3$)$_2$ as the precatalyst. The Cp′$_2$LaNR$_2$ solutions remain colorless during the course of the polymerizations. MALDI-TOF analyses of the quenched polymerization mixtures indicate no significant oligomeric ethylene insertion products or Si–N alcoholysis products; however, GC-MS analysis indicates monoethylene insertion products in ~30–40% yield (eq 4).

Chain-Transfer Efficiency of Primary Amines. Aniline and *n*-propylamine were also investigated as chain-transfer agents using Cp′$_2$LaCH(SiMe$_3$)$_2$ as the precatalyst. *In situ*-generated Cp′$_2$LaNHR complexes are colorless, and reaction solutions

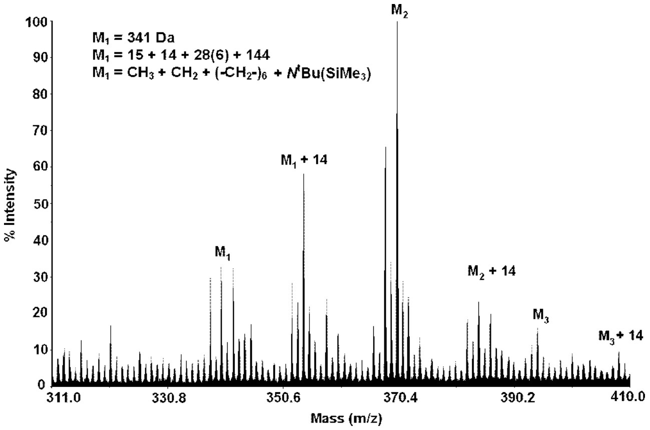
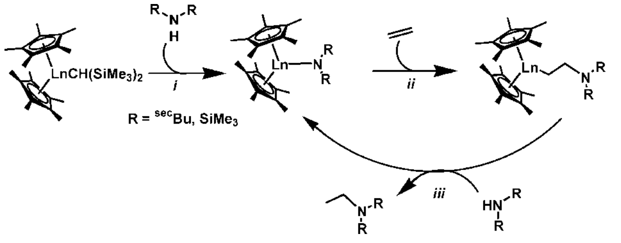


Figure 5. MALDI-TOF mass spectrum of an *N-tert*-butyl(trimethylsilyl)amine-capped oligoethylene produced by Cp′$_2$La-mediated ethylene polymerization in the presence of *N-tert*-butyl(trimethylsilyl)amine.



(4)

remain colorless during the course of the polymerization. The MALDI-TOF, GC-MS, and ^{1}H NMR analyses of the quenched polymerization mixtures indicate no detectable ethylene insertion products.

Secondary Amine Chain-Transfer Efficiency in Organotitanium-Mediated Olefin Polymerizations. Dicyclohexylamine and di-isopropylamine were investigated as chain-transfer agents for CGCTiMe$_2$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$-mediated ethylene and propylene homopolymerizations. All polymerizations were performed under 1.0 atm monomer pressure with [olefin] held constant and the chain-transfer agent maintained in pseudo-zero-order excess. The orange active catalyst solutions remain brightly colored throughout the course of the polymerization reactions, suggesting the presence of a stable active species. CGCTiMe$_2$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$-mediated ethylene polymerizations in the presence of dicyclohexylamine produce small amounts (~30–40 mg) of product polymers with activities up to 10^4 g polymer/(mol of Ti·atm monomer·h). ^{1}H NMR spectra of the product dicyclohexylamine-terminated polyethylenes exhibit characteristic $-CH_2N$, $-CHN$ amine (δ 2.3, 3.1, respectively), $-CH_2-$ polyethylene backbone (δ 1.2–1.5), and $-CH_3$ chain end (δ 0.97) resonances (Figure S2), while the absence of vinylic resonances argues that chain termination via β-hydride elimination is insignificant. Additionally, ^{1}H NMR spectra of the product dicyclohexylamine-terminated polypropylenes produced by CGCTiMe$_2$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ exhibit characteristic $-CH_2N$, $-CHN$ amine (δ 2.4, 3.5, respectively), $-CH_2-$ backbone (δ 1.1–1.3), $-CH$ backbone (δ 1.7), and $-CH_3$ backbone and chain end (δ 0.95) resonances (Figure S3). The absence of olefinic resonances again argues that β-hydride elimination is insignificant. Interestingly, CGCTiMe$_2$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$-mediated olefin polymerizations in the presence of di-isopropylamine produce no detectable insertion products by GC-MS, and CGCTiMe$_2$/Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$-mediated 1-hexene polymerizations in the presence of dicyclohexylamine also yield no detectable insertion products by GC-MS.

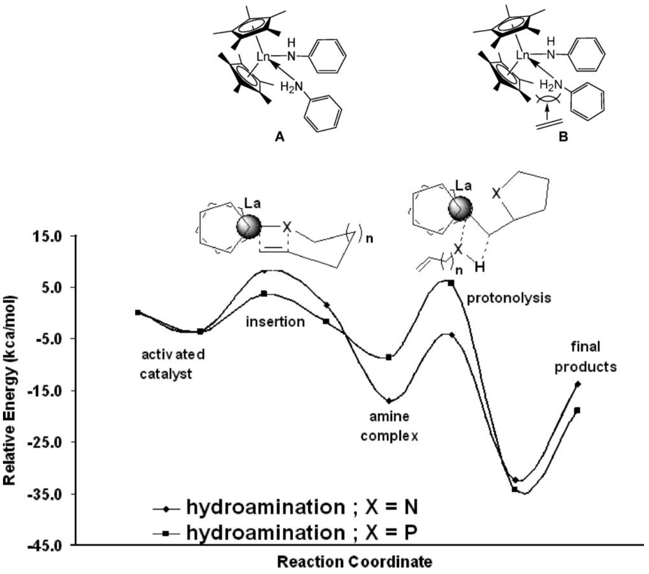


Figure 6. Hydrophosphination/cyclization SCF energy profile compared with that for analogous hydroamination/cyclization. The labeling is for the hydroamination case. Adapted from ref 24.

Discussion

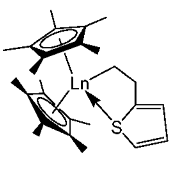
As a prelude to discussing polymerization kinetics and mechanism in the presence of amines, it is useful to outline key constraints on the present catalytic processes: (1) the olefin activation/insertion barrier must be adequately low to allow ethylene insertion into the Ln−amido bond at acceptable rates (step *i*, Scheme 1); (2) if initial insertion is viable, subsequent insertions must be faster than chain-terminating protonolysis for efficient polymer chain growth (step *ii*, Scheme 1); (3) if ethylene insertion is rapid, then chain-terminating protonolysis rates must be sufficient to control the product polymer chain length (step *iii*, Scheme 1). We summarize the interplay of these processes here and discuss their dependence on amine steric and electronic properties. Additionally, we compare and contrast analogous polymerization/chain-transfer processes involving phosphines to better understand the present trends.

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

$$C_6H_5NH_2 \approx C_3H_7NH_2\ (Si(CH_3)_3)_2NH \approx {}^{sec}Bu_2NH > N\text{-}{}^tBu(Si(CH_3)_3)NH \approx {}^iPr_2NH > Cy_2NH$$

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

Step *i*. Unlike lanthanocene-mediated polymerizations conducted in the presence of secondary alkyl- and alkylsilylamines, primary amines aniline and *n*-propylamine produce no detectable ethylene insertion products (Scheme 1, step *i*). Since these amines are the sterically least encumbered of those investigated, it is reasonable that a coordinatively saturated Ln-amido-amine complex[18] is kinetically inert with respect to ethylene insertion (Scheme 1, step *i* rate ≪ step *iii* rate; representative structures **A** and **B** for the aniline case). Additionally, DFT/B3LYP level



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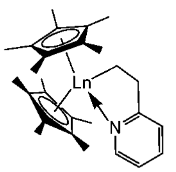

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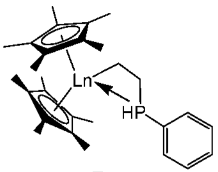

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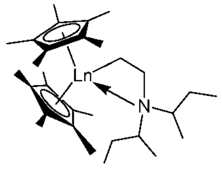

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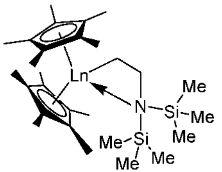
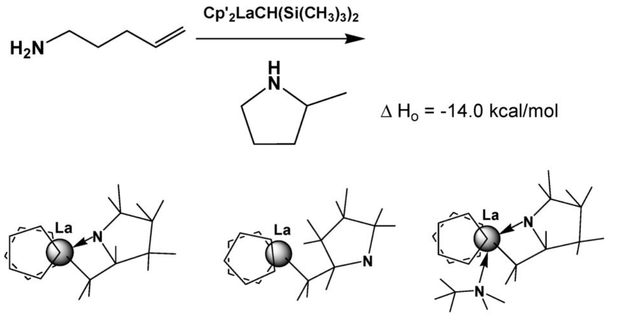


G

theoretical calculations on hydrofunctionalization processes indicate that Ln-NR$_2$ complexes have higher olefin insertion barriers than do Ln-PR$_2$ complexes (ΔH ~5 kcal/mol, Figure 6),[23,24] while calorimetrically determined thermochemical data indicate that the Sm−N bond enthalpy in Cp′$_2$Sm−NMe$_2$ (~48 kcal/mol) is far greater than the Sm−P bond enthalpy in Cp′$_2$Sm−PEt$_2$(ΔH ~32 kcal/mol).[22a]

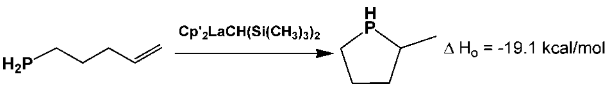
Step *ii*. Regarding the frequent observation of monoinsertion products here, note that for thiophene,[10] pyridine,[17] and phenylphosphine chain-transfer agents,[8] monoinsertion products are found to be particularly stable toward further ethylene insertion, likely a consequence of intramolecular heteroatom coordination to the electrophilic Ln center (e.g., **C**−**E**). Therefore, it is possible in the present case that the monoinsertion products Cp′$_2$LaCH$_2$CH$_2$N^{sec}Bu$_2$ and Cp′$_2$LaCH$_2$CH$_2$N(Si(CH$_3$)$_3$)$_2$ are also less reactive toward ethylene insertion due to stabilizing intramolecular amine coordination (e.g., **F** and **G**, respectively; step *ii* rate ≪ step *i* rate, Scheme 1). In this connection, the DFT/B3LYP computational studies on the geometries and stabilities of the intermediates and transition states in organolanthanide-catalyzed hydroamination/cyclization of 1-aminopent-4-ene (eq 5) find two stable product conformations, **H** and **I**, following initial intramolecular olefin insertion into the La−N bond.[23]



H **I** **J**

(5)

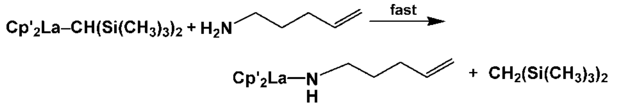
Chelating conformation **H** is computed to be ~16.4 kcal/mol more stable than **I**, whereas intermolecular coordination of free, nonbulky methylamine accrues an additional ~18 kcal/mol stabilization for **J** versus **I**. These calculations therefore suggest that the monoinsertion products **F** and **G** are likely stabilized by the intramolecular amine coordination.



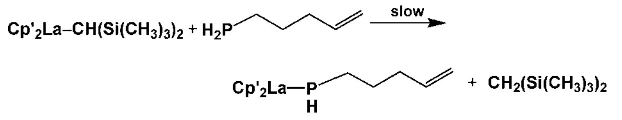
(6)

DFT/B3LYP analysis of the functionally analogous organolanthanide-catalyzed hydrophosphination/cyclization of 1-phosphinopent-4-ene (eq 6) reveals both differences and similarities between N and P.[23] Geometry optimizations of the phosphine cyclization products reveal two stable conformations (**K** and **L**), similar to the aforementioned hydroamination results.[24] Conformation **K** involves P-coordination to the La center and is computed to be 13.1 kcal/mol more stable than **L**, and again coordination of nonbulky free methylphosphine yields a phosphine-phosphido complex with ~7 kcal/mol additional stabilization (**M**) versus **L**. As a likely consequence, the present systems implementing di-*sec*-butyl- and *N*,*N*-bis(trimethylsilyl)amine most frequently afford monoinsertion products.

Step *iii*. Theoretical and experimental evidence both indicate rapid, quantitative Ln-alkyl precatalyst protonolysis with amines (eq 7, Figure 6) in contrast to more sluggish phosphine protonolysis (eq 8, Figure 6).[8,17] Invoking hard/soft acid–base concepts, these different protonolysis rates may reflect the “softer” nature of P versus N,[25] despite the greater Brønsted acidity of R$_2$PH versus R$_2$NH.[26] Thus, the experimental and theoretical results argue that alkene insertion is turnover-limiting for hydroamination, while Ln−C bond protonolysis is turnover-limiting for hydrophosphination, in excellent agreement with the more facile chain growth observed in phosphine polymerization/chain-transfer systems.[8]



(7)



(8)

The protonolytic Ln−C bond cleavage rate is likely governed by amine reagent steric bulk and Brønsted acidity (Scheme 1, step *iii*). The experimental solution-phase Brønsted acidity of the amine chain-transfer agents investigated here decreases in the order[26]

$$C_6H_5NH_2 > C_3H_7NH_2/(Si(CH_3)_3)_2NH > N\text{-}^tBu(Si(CH_3)_3)NH > Cy_2NH/^{sec}Bu_2NH \approx {}^iPr_2NH$$

As noted above, the product polymer M_n values reflect the rates governing chain growth in Scheme 1, steps *i* and *ii* (k^{ethylene}) counterbalanced by the rates of competing step *iii* protonolysis (k^{NH}). Thus, di-isopropyl- and *N*-*tert*-butyl(trimethylsilyl)amine are moderately efficient protonolytic chain-transfer agents and produce amine-capped oligoethylenes in reasonable yields (rates *i*/*ii* > rate *iii*). However, only with an appropriate balance of steric and electronic properties can

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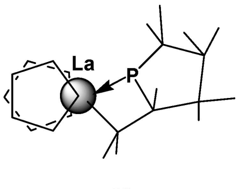
(23) Motta, A.; Lanza, G.; Fragala, I. L.; Marks, T. J. *Organometallics* **2004**, *23*, 4097.

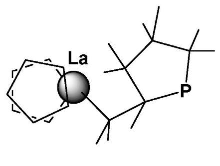
(24) Motta, A.; Fragala, I. L.; Marks, T. J. *Organometallics* **2005**, *24*, 4995.

(25) Pearson, R. G. *J. Chem. Educ.* **1987**, *64*, 561.

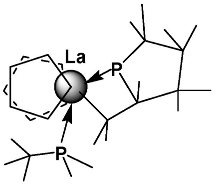
(26) Relative Brønsted acidities: (a) Koppel, I. A.; Burk, P.; Koppel, I.; Leito, I. *J. Am. Chem. Soc.* **2002**, *124*, 5594. (b) Koppel, I. A.; Burk, P.; Koppel, I.; Leito, I.; Sonoda, T.; Mishima, M. *J. Am. Chem. Soc.* **2000**, *122*, 5114.



K

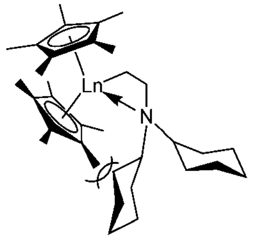


L

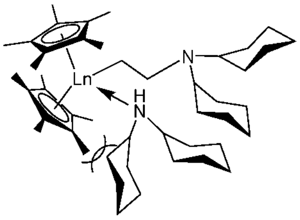


M

efficient chain propagation occur before chain-growth termination (rates *i*/*ii* > > rate *iii*), such as for dicyclohexylamine (Table 1). Lanthanocene-mediated (La, Sm) ethylene polymerizations in the presence of dicyclohexylamine result in high M_n polyethylenes, likely reflecting the increased amine steric bulk and decreased secondary amine Brønsted acidity. This also suggests that steric repulsions in monoinsertion products **N** and **O** may render intramolecular or intermolecular amine coordination less favorable versus the other amines investigated. The Cp'_2La- and Cp'_2Sm-catalysts produce dicyclohexylamine-terminated polyethylenes with relatively high productivities, whereas Cp'_2Y- and Cp'_2Lu-mediated systems are less efficient, producing only trace amounts of polymer, paralleling known trends in $Cp'_2Ln\text{-}NR_2$ olefin insertion reactivity with falling ionic radius (see more below).[19]



N



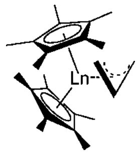
O

The organotitanium-mediated ethylene and propylene homopolymerizations conducted here in the presence of secondary amines result in small quantities of product polymers, likely reflecting the relative inertness of the $Ti^+{-}NR_2$ bond and/or the greater stability of structures such as **O** for cationic d^0 centers.[23b] Addition of dicyclohexylamine to the Ti-mediated systems allows rapid C=C propagation prior to chain termination with productivities up to 10^4 g polymer/(mol Ti·atm monomer·h), likely a consequence of slow chain transfer for this sterically encumbered amine. However, less bulky diisopropylamine results in no detectable insertion products, presumably due to slow C=C insertion. The rates of propagation of higher α-olefins, such as 1-hexene, are too slow to effect chain growth, resulting in no detectable insertion products. Thus, organotitanium polymerization systems produce amine-functionalized polyolefins, albeit with currently limited scope and efficiency.

Lanthanide Ionic Radius and Chain-Transfer Reactivity. The present lanthanide ionic radius−polymerization activity trend parallels that of small-molecule hydroamination[19] and ethylene homopolymerization[15] (Table 1, entries 1–4), indicating more facile C=C enchainment

$$\mathrm{Cp_2'La-} > \mathrm{Cp_2'Sm-} > \mathrm{Cp_2'Y-} \approx \mathrm{Cp_2'Lu-}$$

in the coordination spheres of larger lanthanide ions (La^{3+}, Sm^{3+})[15] and also steric constraints around the smaller ions (Y^{3+}, Lu^{3+}). Interestingly, larger La^{3+} produces slightly lower molecular weight polymers versus those produced with Sm^{3+}, likely reflecting the sensitive steric demands and competition between ethylene insertion/propagation (k_p^{ethylene}) versus protonolytic chain transfer (k_t^{NH}; Table 1, entries 3 and 4). Thus, larger La^{3+} mediates somewhat more rapid ethylene propagation versus smaller Sm^{3+}, k_p^{ethylene} (La^{3+}) > k_p^{ethylene} (Sm^{3+}), but also slightly more rapid protonolytic chain transfer, k_t^{NH} (La^{3+}) > k_t^{NH} (Sm^{3+}). Regardless of lanthanide ion, propylene homopolymerizations in the presence of dicyclohexylamine afford no detectable olefin insertion products. One possible explanation lies in facile documented organolanthanide-mediated propylene C−H activation processes.[10,15,17,27,28] η^3-Allyl species (**P**) are expected to be less reactive with respect to propylene insertion and may undergo protonolysis to regenerate the corresponding amido complex.[22] That Cp'_2LnNCy_2-mediated 1-hexene homopolymerizations in the presence of amines also afford no detectable insertion products is presumably due to such unfavorable C−H activation processes or to sluggish insertion rates for the more sterically encumbered monomer.



P

Kinetics and Mechanism. The catalytic system Cp'_2LaNCy_2 + $HNCy_2$ + ethylene produces dicyclohexylamine-capped polyethylenes over a wide range of amine concentrations (Table 1, entries 5–9). A series of polymerizations with varying dicyclohexylamine concentrations (in pseudo-zero-order excess) was conducted using Cp'_2LaNCy_2 as the catalyst and with constant [catalyst] and [ethylene] and rapid mixing. Under these conditions, a linear relationship between M_n and [dicyclohexylamine]$^{-1}$ is observed (Figure 3), consistent with amine chain termination being the dominant pathway. The absence of vinyl ^{1}H NMR resonances in the product polymer and the ~1:1 $-CH_3$:$-CH_2N$ chain end ratio also supports protonolysis as the dominant chain-transfer pathway (Figure 1, Scheme 1). Under steady-state conditions, the number-average degree of polymerization, P_n, is equal to the sum of all rates of propagation, $\sum R_p$, divided by the rates of all competing chain-transfer pathways, $\sum R_t$ (eq 9).[8,9] Assuming a single dominant chain-transfer process by amine protonolysis and rapid chain reinitiation after chain transfer, P_n is given by eq 10, where k_p is the

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(27) C−H activation mediated by organolanthanide complexes: (a) Evans, W. J.; DeCoster, D. M.; Greaves, J. *Organometallics* **1996**, *15*, 3210. (b) Deelman, B.-J.; Booij, M.; Meetsma, A.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1995**, *14*, 2306. (c) Booij, M.; Deelman, B.-J.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 3531. (d) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134. (e) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314. (f) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (g) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337.

(28) (a) Dahlmann, M.; Erker, G.; Bergander, K. *J. Am. Chem. Soc.* **2000**, *122*, 7986. (b) Karl, J.; Dahlmann, M.; Erker, G.; Bergander, K. *J. Am. Chem. Soc.* **1998**, *120*, 5643. (c) Kissin, Y. V. *Isospecific Polymerization of Olefins*; Springer-Verlag: New York, 1985; pp 1–93.

rate constant for propagation and k_t^{NH} is the rate constant for intermolecular amine chain transfer.

$$\bar{P}_n = \frac{\sum R_p}{\sum R_t} \tag{9}$$

$$\bar{P}_n = \frac{k_p^{ethylene}[\text{ethylene}]}{k_t^{NH}[\text{amine}]} \tag{10}$$

With a series of polymerizations carried out at constant [catalyst] and [monomer] and with [dicyclohexylamine] in pseudo-zero-order excess, Figure 3 shows that eq 10 is obeyed over a broad [amine] range. Using eq 10 and the data in Figure 3 yields the $k_p^{\text{ethylene}}/k_t^{NH}$ rate constant ratio. For the present system $k_p^{\text{ethylene}}/k_t^{NH} \approx 1700$, approximately 10 times the ratios observed for the Cp'_2YPPh_2- ($k_p^{\text{ethylene}}/k_{\text{phosphine}} \approx 200$, diphenylphosphine),[8b] $[Cp'_2SmH]_2$- ($k_p^{\text{ethylene}}/k_{\text{Si}} \approx 190$, phenylsilane),[5e] and $CGCTiMe_2/PhC^+B(C_6F_5)_4^-$-mediated ($k_p^{\text{ethylene}}/k_{\text{Si}} \approx 180$, 5-hexenylsilane)[5b,c] polymerization systems. The present large $k_p^{\text{ethylene}}/k_t^{NH}$ ratio is consistent with the exceptionally high product polymer molecular weights, which are ~10 times those reported in the aforementioned systems using phosphine and silane chain-transfer agents at similar concentrations. In the present systems, product molecular weights rival those produced in the absence of chain-transfer agent.[15] The single-site character of the present systems is completely consistent with the aforementioned good activities, high product molecular weights, and narrow polydispersities ($M_w/M_n \approx 2.0$), in accord with the scenario of Scheme 1.

Conclusions

This investigation demonstrates that amines can act as efficient Ln−C cleaving/C−N bond-forming chain-transfer agents in Cp'_2Ln-mediated ethylene polymerizations. The overall efficiency of chain transfer in lanthanocene-mediated ethylene polymerizations increases in the order

$$C_6H_5NH_2 \approx C_3H_7NH_2\ (Si(CH_3)_3)_2NH \approx {}^{sec}Bu_2NH < N\text{-}{}^tBu(Si(CH_3)_3)NH \approx {}^iPr_2NH < Cy_2NH$$

Primary amines are least efficient and do not yield insertion products, likely due to strong amine/amide binding to the Ln^{3+} center and the high resulting olefin insertion barrier. Among secondary amines, *N*,*N*-bis(trimethylsilyl)amine and di-*sec*-butylamine are the least efficient chain-transfer agents, producing only monoethylene insertion products. *N*-*tert*-butyl(trimethylsilyl)amine and di-isopropylamine are also efficient chain-transfer agents for Cp'_2La-mediated polymerizations, producing oligoethylene products. Dicyclohexylamine is the most effective chain-transfer agent found for lanthanocene-mediated ethylene polymerizations, producing high molecular weight linear, chain-end-functionalized polymeric products.

A series of Cp'_2LaCy_2-mediated polymerizations with varying amine concentrations was carried out and reveals good polymerization rates, high product polymer molecular weights, $M_w/M_n \approx 2.0$, negligible β-hydride elimination NMR resonances, a 1:1 ratio of CH_3:CH_2N chain end units, and a linear relationship between M_n and $[\text{dicyclohexylamine}]^{-1}$, all consistent with a predominant protonolytic, amine chain-transfer mechanism. Due to the complex interplay of insertion, propagation, and protonolysis rates, careful optimization of amine steric and electronic properties is necessary to afford high molecular weight heteroatom-functionalized polymers.

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Supporting Information Available: Detailed analytical data for polymeric/oligomeric products (Figures S1–S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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