

In Situ Formation of Bis(phosphinimino)methanide Rare Earth Alkoxide Initiators for the Ring-Opening Polymerization of ϵ -Caprolactone

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A series of pentamethylcyclopentadienyl bis(phosphinimino)methanide complexes of yttrium and the lanthanides, $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{Ln}(\eta^5\text{-C}_5\text{Me}_5\text{Cl})]$ (Ln = Y (**1a**), Sm (**1b**), Yb (**1c**)), were prepared by two different synthetic approaches. The compounds can be obtained either from $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{LnCl}_2]_2$ (Ln = Y, Sm, Yb) and $\text{K}(\text{C}_5\text{Me}_5)$ or in a one-pot reaction when $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$ is reacted with anhydrous rare earth trichlorides in the presence of $\text{K}(\text{C}_5\text{Me}_5)$. When **1a–c** were combined in situ with 1 equiv of 2-propanol, an active $[\text{Ln}]\text{-O}i\text{Pr}$ initiator was formed that enabled the pseudo-living ring-opening polymerization of ϵ -caprolactone to polymers with controlled molecular features (end groups, \bar{M}_n) and very narrow molar mass distributions.

Introduction

Aliphatic polyesters have attracted major interest by virtue of their biodegradability and biocompatibility properties.^{1,2} Rare earth metal complexes have displayed high polymerization activity toward a wide variety of monomers, including both polar and nonpolar species.¹ Following the pioneering work of McLain, rare earth derivatives are now being widely used for the ring-opening polymerization (ROP) of cyclic esters, especially diesters and lactones, leading to biodegradable and biocompatible polyesters.^{1–3} In this field, in addition to some novel complexes such as the borohydrides, alkoxide initiating systems remain the most common.^{4,5} Literature results on various rare earth initiators used for the ROP of lactones have also revealed the key role played by the ancillary ligands, the steric bulkiness of which seems to limit side reactions in preventing access to the metal center.^{4a,5a,6} The design of novel initiators for living and controlled polymerizations thus nowa-

days involves bulky ligands of the post-metallocene type, essentially polydentate N-, O-, and P-donor ligands.^{1b,6,7} The impact of single-site initiators in better controlling the polymer features has also been highlighted.^{4a,5a,6} Even though a large number of rare earth initiators have been reported so far, to the best of our knowledge, only very few systems initiate the polymerization of ϵ -CL to give polyesters with extremely narrow molar mass distributions. The lanthanide metallocene alkyls and hydrides $[(\text{C}_5\text{Me}_5)_2\text{Sm}-\text{CH}_3(\text{THF})]$ and $[(\text{C}_5\text{Me}_5)_2\text{Sm}-\text{H}]_2$ and the alkoxides $[(\text{C}_5\text{Me}_5)_2\text{Sm}-\text{OEt}(\text{OEt}_2)]$, $[(\text{C}_5\text{H}_5)_2\text{Y}-\text{OCH}_3]_2$, $[(\text{C}_5\text{Me}_5)_2\text{Y}-\text{OCH}_3(\text{THF})]$, $[(\text{Me}_3\text{SiCH}_2)_2\text{Y}-\text{O}(\text{C}_6\text{H}_5-2,6\text{-tBu}_2\text{-THF})_2]$, and $[(\text{EA})_2\text{Ln}-\text{O}i\text{Pr}]$ (EA = ethyl acetoacetate) initiate the living polymerization of ϵ -CL to give polyesters with molar mass distributions among the lowest ever reported with organo-rare earth initiators ($\bar{M}_w/\bar{M}_n < 1.10$).^{6c,8}

We report here on novel and relatively robust organometallic lanthanide halide precatalysts of the composition $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{Ln}(\eta^5\text{-C}_5\text{Me}_5\text{Cl})]$ (Ln = Y, Sm, Yb) for the polymerization of ϵ -CL to give polyesters with very narrow molar mass distributions. The synthesis of the complexes is based on our recently developed concept of using, as spectator ligand, the very bulky bis(phosphinimino)methanide $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$, which can direct the substitution pattern on the lanthanide atom just by its steric demand and constraint.

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We previously reported the synthesis of a series of lanthanide bis(phosphinimino)methane dichloride complexes, including yttrium: $\{[\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2]\text{LnCl}_2\}_2$ (Ln = Y, Sm, Dy, Er, Yb, Lu).^{9a} These compounds were obtained by the reaction of $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^{\text{9b}}$ with the corresponding yttrium or lanthanide trichlorides. We now use $\{[\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2]\text{LnCl}_2\}_2$ as the starting material in a modular approach. Depending on the steric demand of further substituents (L), the complexes $\{[\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2]\text{Ln}(\text{L})\text{Cl}\}$ or $\{[\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2]\text{LnL}_2\}$ were recovered with bulky or relatively small coligands, respectively.^{9a,c,d}

Experimental Section

General Considerations. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high-vacuum (10^{-4} Torr) line, or in an argon-filled M. Braun glovebox. Ether solvents (THF and ethyl ether) were predried over Na wire and distilled under nitrogen from K (THF) or Na wire (ethyl ether) as well as benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from LiAlH_4 . All solvents for vacuum line manipulations were stored in vacuo over LiAlH_4 in resealable flasks. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH (all ≥ 99 atom % D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. ϵ -Caprolactone (ϵ -CL, Lancaster) was successively dried over CaH_2 (at least 1 week) and then over 4,4'-methylenebis(phenyl isocyanate). HOiPr (Aldrich) was dried over molecular sieves (4 Å). LnCl_3 ,¹⁰ $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^{\text{9b}}$ and $\{[\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2]\text{LnCl}_2\}_2^{\text{9a}}$ were prepared according to literature procedures.

Instrumentation and Measurements. ^1H NMR spectra were recorded on a Bruker AC 250, a Jeol JNM-LA 400 FT-NMR, or an Avance DPX 400 spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and 85% phosphoric acid (^{31}P NMR), respectively. IR spectra were obtained on a Shimadzu FTIR-8400s instrument. Mass spectra were recorded on a Varian MAT 711 spectrometer. Elemental analyses were carried out with an Elementar vario EL instrument. Molar masses (\bar{M}_n) and molar mass distributions (\bar{M}_w/\bar{M}_n) determinations were performed by size exclusion chromatography (SEC) in THF at 20 °C (flow rate 1.0 mL min^{-1}) on a Jasco apparatus equipped with a refractive index detector and one Polymer Laboratory column with 5 μm particle size. The polymer samples were dissolved in THF (2 mg \cdot mL $^{-1}$). The very narrow molar mass distribution values obtained under such conditions are even narrower under optimized experimental analysis conditions (Varian apparatus equipped with three TSK HXL columns with successively 5000, 3000, and 2000 Å pore sizes, flow rate 0.8 mL min^{-1}) as exemplified by the PCL obtained in Table 2, run 6 ($\bar{M}_n(\text{SEC}) = 38\,700$ with $\bar{M}_w/\bar{M}_n = 1.20$), which then gives $\bar{M}_n(\text{SEC}) = 37\,300$ with $\bar{M}_w/\bar{M}_n = 1.15$. Average molar mass values were calculated from the linear polystyrene calibration curve using the correction coefficient previously reported $[0.56(\bar{M}_n(\text{exptl})] = \bar{M}_n(\text{SEC})$.^{4,19c} The monomer conversion was calculated from the ^1H NMR spectrum of the crude polymer sample after the integration (int) ratio $\text{int}(\text{P}(\text{CL}))/[\text{int}(\text{P}(\text{CL})) + \text{int}(\text{CL})]$ using the $\text{CH}_2\text{OC}(\text{O})$ methylene triplet (δ 4.04). MALDI-TOF MS experiments were

performed by the CESAMO (Bordeaux, France) and carried out on a Reflex apparatus (Bruker) equipped with a pulsed N_2 laser (337 nm, 4 ns pulse width) and time-delayed extracted ion source. Spectra were recorded in the positive ion mode using the reflectron mode and an accelerating voltage of 20 kV. Polymer samples were dissolved in THF (10 mg mL^{-1}), and ditranol/THF (10 mg mL^{-1}) and NaI/MeOH solutions (10 mg mL^{-1}) were prepared as the matrix and cation source, respectively. All three solutions were then mixed in a 1:10:1 volume ratio, respectively, deposited on the sample target, and then air-dried.

$\{[\text{C}_5\text{SiNPPPh}_2)_2\text{CH}\}\text{Ln}(\text{C}_5\text{Me}_5\text{Cl})$ (Ln = Y (**1a**), Sm (**1b**), Yb (**1c**)) (General Procedure). **Route A.** THF (20 mL) was condensed at -196 °C onto a mixture of $\{[\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2]\text{LnCl}_2\}_2$ (0.5 mmol) and $\text{K}(\text{C}_5\text{Me}_5)$ (175 mg; 1.0 mmol), and the mixture was stirred for 18 h at room temperature. The mixture was refluxed for a short period (30 min) and filtered, and the solvent was taken off in vacuo. The product was isolated after recrystallization from toluene.

Route B. THF (20 mL) was condensed at -196 °C onto a mixture of $\{[\text{C}_5\text{SiNPPPh}_2)_2\text{CH}\}\text{K}$ (328 mg, 0.55 mmol), LnCl_3 (0.5 mmol), and KC_5Me_5 (88 mg, 0.5 mmol), and the mixture was stirred for 18 h at room temperature. The mixture was then refluxed for a short period (30 min) and filtered, and the solvent was taken off in vacuo. The product was isolated after recrystallization from toluene.

1a (Ln = Y, Routes A and B). Yield: 285 mg (66%, route B), colorless crystals. ^1H NMR ($[\text{D}_8]\text{THF}$, 250 MHz, 25 °C): δ 0.19 (s, 18H; SiMe₃), 1.73 (s, 15H; C₅Me₅), 1.96 (m, 1H; CH), 2.30 (s, 1.5H; toluene), 6.87–6.94 (m, 4H; Ph), 7.05–7.39 (m, 8.5H; Ph + toluene), 7.52–7.60 (m, 6H; Ph), 7.91–7.99 (m, 4H; Ph). ^{29}Si NMR ($[\text{D}_8]\text{THF}$, 49.7 MHz, 25 °C): δ -2.3. $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$, 101.3 MHz, 25 °C): δ 18.8 (d, $^2J(\text{P},\text{Y}) = 6.9$ Hz). MS (70 eV, EI): m/z (%) 816 (0.7) $[\text{M}]^+$, 801 (3.2) $[\text{M} - \text{Me}]^+$, 681 (100) $[\text{M} - \text{C}_5\text{Me}_5]^+$, 543 (7) $[\text{C}_{30}\text{H}_{36}\text{N}_2\text{P}_2\text{Si}_2]^+$. Anal. Calcd for $\text{C}_{89}\text{H}_{116}\text{Cl}_2\text{N}_4\text{P}_4\text{Si}_4\text{Y}_2$ ((**1a**)₂·(toluene), 1726.82): C, 61.90; H, 6.77; N, 3.24. Found: C, 61.70; H, 6.68; N, 3.25.

1b (Ln = Sm, Routes A and B). Yield: 365 mg (79%, route B), yellow-orange crystals. ^1H NMR ($[\text{D}_8]\text{THF}$, 250 MHz, 25 °C): δ -1.51 (s, 18H; SiMe₃), 1.15 (s, 15H; C₅Me₅), 2.30 (s, 1.5H; toluene), 5.74 (br, 1H; CH), 6.18 (br, 4H; Ph), 6.95–7.01 (m, 4H; Ph), 7.10–7.23 (m, 4.5H; Ph + toluene), 7.65–7.68 (m, 6H; Ph), 9.31 (br, 4H; Ph). ^{29}Si NMR ($[\text{D}_8]\text{THF}$, 49.7 MHz, 25 °C): δ -1.5. $^{31}\text{P}\{^1\text{H}\}$ NMR ($[\text{D}_8]\text{THF}$, 101.3 MHz, 25 °C): δ 41.7. MS (70 eV, EI): m/z (%) 879 (0.5) $[\text{M}]^+$, 864 (0.8) $[\text{M} - \text{Me}]^+$, 844 (100) $[\text{M} - \text{C}_5\text{Me}_5]^+$, 543 (33) $[\text{C}_{30}\text{H}_{36}\text{N}_2\text{P}_2\text{Si}_2]^+$. Anal. Calcd for $\text{C}_{89}\text{H}_{116}\text{Cl}_2\text{N}_4\text{P}_4\text{Si}_4\text{Sm}_2$ ((**1b**)₂·(toluene), 1849.7): C, 57.79; H, 6.32; N, 3.03. Found: C, 57.56; H, 6.29; N, 2.87.

1c (Ln = Yb, Route A). Yield: 674 mg (71%), purple crystals. IR (KBr): ν 3062 (m), 2949 (m), 2893 (m), 2853 (m), 1436 (s), 1251 (m), 1240 (m), 1128 (s), 1081 (m), 847 (m), 766 (s) cm^{-1} . MS (70 eV, EI): m/z (%) 902 (12) $[\text{M}]^+$, 888 (26) $[\text{M} - \text{Me}]^+$, 766 (100) $[\text{M} - \text{C}_5\text{Me}_5]^+$, 543 (24) $[\text{C}_{30}\text{H}_{36}\text{N}_2\text{P}_2\text{Si}_2]^+$. Anal. Calcd for $\text{C}_{89}\text{H}_{116}\text{Cl}_2\text{N}_4\text{P}_4\text{Si}_4\text{Yb}_2$ ((**1c**)₂·(toluene), 1895.8): C, 56.41; H, 6.17; N, 2.96. Found: C, 56.62; H, 6.15; N, 2.91.

X-ray Crystallographic Studies of 1a–c. Crystals of **1a–c** were grown from toluene. A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the -73 or -100 °C N_2 cold stream of a Stoe IPDS or a Stoe IPDS 2T diffractometer. Subsequent computations were carried out on an Intel Pentium IV PC.

All structures were solved by the Patterson method (SHELXS-97).¹¹ The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F_o , minimizing the function $(F_o - F_c)^2$, where the weight is defined

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Table 1. Crystallographic Details of $[\{\text{Me}_3\text{SiNPPH}_2\}_2\text{CH}\}\text{Ln}(\text{C}_5\text{Me}_5)\text{Cl}$ (Ln = Y (1a**), Sm (**1b**), Yb (**1c**))^a**

	(1a) ₂ ·(toluene)	(1b) ₂ ·(toluene)	(1c) ₂ ·(toluene)
formula	C ₈₉ H ₁₁₆ Cl ₂ N ₄ P ₄ Si ₄ Y ₂	C ₈₉ H ₁₁₆ Cl ₂ N ₄ P ₄ Si ₄ Sm ₂	C ₈₉ H ₁₁₆ Cl ₂ N ₄ P ₄ Si ₄ Yb ₂
formula wt	1726.82	1849.7	1895.08
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> , Å	20.8649(10)	20.9738(13)	20.731(2)
<i>b</i> , Å	15.6124(8)	15.6568(8)	15.476(2)
<i>c</i> , Å	14.6317(9)	14.6019(9)	14.536(2)
β , deg	105.547(6)	105.776(7)	105.870(8)
<i>V</i> , Å ³	4591.9(4)	4614.4(5)	4485.9(8)
<i>Z</i>	2	2	2
density (g/cm ³)	0.806	1.331	1.403
radiation	Ag K α (λ = 0.806 Å)	Ag K α (λ = 0.806 Å)	Mo K α (λ = 0.710 73 Å)
μ , mm ⁻¹	1.249	0.792	2.301
abs cor	none	none	integration
no. of rflns collected	38 476	46 628	19 558
no. of unique rflns	14 482 (<i>R</i> _{int} = 0.1137)	11 565 (<i>R</i> _{int} = 0.0351)	7850 (<i>R</i> _{int} = 0.0330)
no. of obsd rflns	8434	9701	6463
GOF on <i>F</i> ²	1.037	1.065	1.021
<i>R</i> ₁ , ^b <i>wR</i> ₂ ^c	0.0746, 0.1868	0.0371; 0.1068	0.0285; 0.0647

^a All data collected at 203 K. ^b *R*₁ = $\sum(|F_o| - |F_c|)/\sum|F_o|$. ^c *wR*₂ = $[\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$.

as $4F_o^2/2(F_c^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, using the program SHELXL-97.¹² In the final cycles of each refinement, all non-hydrogen atoms except C31–C35 and the toluene molecules in **1a–c** were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded, assuming a C–H bond length of 0.95 Å. The hydrogen atom contributions were calculated but not refined. The final values of refinement parameters are given in Table 1. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication Nos. CCDC-609531 (**1a**), CCDC-609532 (**1b**), and CCDC-274505 (**1c**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223-336-033; email, deposit@ccdc.cam.ac.uk).

Typical Polymerization Procedure. Compound **1a** (17.1 mg, 20.90 μmol) was initially dissolved in THF (1 mL) and stirred with HO*i*Pr (1 equiv, 1.6 μL). After 15 min ϵ -CL (0.5 mL, 4.51 mmol) in THF (2.5 mL) was added and the clear solution stirred. The reaction was then quenched with an acetic acid solution. The resulting mixture was dried and the conversion determined by ¹H NMR analysis. This crude polymer was dissolved in CH₂Cl₂,

purified upon precipitation in a large amount of cold pentane, and finally dried under dynamic vacuum. The recovered polymers were then characterized by ¹H and ¹³C NMR, SEC, and MALDI-TOF analyses.

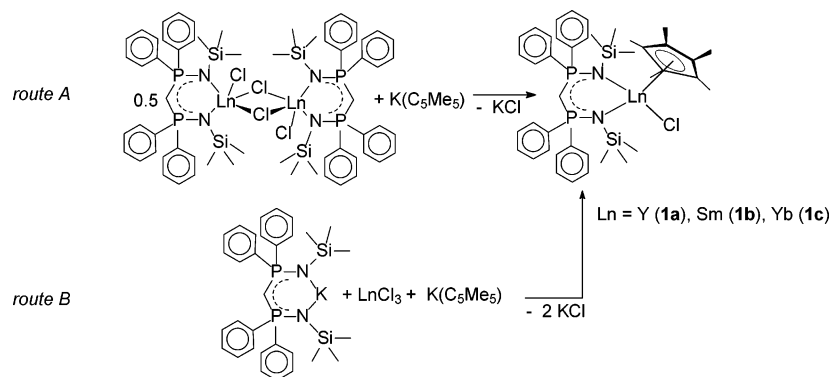
Results and Discussion

Metal Complex Synthesis. The title compounds $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}]$ (Ln = Y (**1a**), Sm (**1b**), Yb (**1c**)) can be obtained by two different synthetic approaches (Scheme 1).¹³ The first route involves the reaction of the well-established lanthanide dichloride compound $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{LnCl}_2]_2$ (Ln = Y, Sm, Yb)^{9b} with $\text{K}(\text{C}_5\text{Me}_5)$ in a 1:2 molar ratio in THF, which affords the corresponding monocyclopentadienyl complexes as crystals in good yields (Scheme 1, route A). A convenient alternative to obtain compounds **1a–c** is the one-pot reaction of the potassium methanide complex $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$ with anhydrous rare earth trichloride and $\text{K}(\text{C}_5\text{Me}_5)$ in a 1:1:1 molar ratio in THF (Scheme 1, route B). The new complexes have been characterized by standard analytical/spectroscopic techniques, and the solid-state structures of all three compounds were established by single-crystal X-ray diffraction.

The ¹H, ²⁹Si{¹H}, and ³¹P{¹H} NMR spectra of the diamagnetic compound **1a** and of the slightly paramagnetic complex **1b** were investigated. The ¹H NMR spectra of compounds **1a,b** show the characteristic sharp singlets of the Me₃Si groups and the triplets of the methine protons of the $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$ ligand. This CH signal in **1a** (δ 1.96 ppm) is in the range of that of the starting material $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{YCl}_2]_2$ (δ 1.93 ppm). In contrast, in the paramagnetic compound **1b** a strong downfield shift of this signal (δ 5.74 ppm) is observed compared to $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{SmCl}_2]_2$ (δ 2.61 ppm). In both **1a** and **1b** the signals of the methine protons are broadened. The phenyl region in the ¹H NMR spectra is as expected. The anticipated characteristic signal for the $\eta^5\text{-C}_5\text{Me}_5$ ring is observed in each compound. Complexes **1a,b** each show one sharp signal in the ³¹P{¹H} NMR spectra (δ 18.8 ppm (**1a**), 41.7 ppm (**1b**)), showing that the phosphorus atoms are chemically equivalent in solution. In the ³¹P{¹H} NMR spectrum of the yttrium complex **1a**, a coupling constant of 6.9 Hz, typical of a ²*J*(P,Y) coupling, is observed.⁹

The solid-state structures of **1a–c** were established by single-crystal X-ray diffraction (Figure 1). Compounds **1a–c** crystallize in the monoclinic space group *P*2₁/*c*, having four molecules of **1** and two molecules of toluene in the unit cell. As a result of the similar ion radii of the metals, the single-crystal X-ray structures of **1a–c** are isostructural. The coordination polyhedron is formed by the η^5 -coordinated cyclopentadienyl ring, the chlorine atom, and the $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$ ligand. The Ln–C

Scheme 1. Synthesis of $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}]$ (1a–c**) via Two Different Routes**



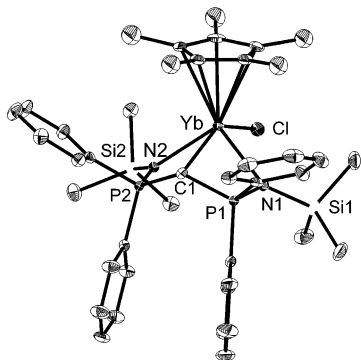


Figure 1. Perspective ORTEP view of the molecular structure of **1c**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) or angles (deg) are as follows (also given for isostructural **1a,b**). **1a:** Y–N1 = 2.401(4), Y–N2 = 2.396(3), Y–Cl = 2.5757(14), Y–C1 = 2.649(4), Y–C_g = 2.386(7), N1–P1 = 1.601(4), N2–P2 = 1.603(3), C1–P1 = 1.734(4), C1–P2 = 1.750(4); N1–Y–N2 = 99.33(12), N1–Y–Cl = 90.62(10), N2–Y–Cl = 96.33(9), N1–Y–C1 = 64.53(13), N2–Y–C1 = 65.01(11), Cl–Y–C1 = 143.98(9), C_g–Y–N1 = 126.56(0), C_g–Y–N2 = 126.64(0), C_g–Y–Cl = 107.48(0), C_g–Y–C1 = 108.48(0), N1–P1–C1 = 108.3(2), N2–P2–C1 = 108.3(2). **1b:** Sm–N1 = 2.458(3), Sm–N2 = 2.461(2), Sm–Cl = 2.6336(9), Sm–C1 = 2.712(3), Sm–C_g = 2.451(9), N1–P1 = 1.600(3), N2–P2 = 1.595(3), C1–P1 = 1.738(3), C1–P2 = 1.745(3); N1–Sm–N2 = 97.32(9), N1–Sm–Cl = 91.36(7), N2–Sm–Cl = 99.03(6), N1–Sm–C1 = 63.11(9), N2–Sm–C1 = 63.30(8), Cl–Sm–C1 = 144.51(6), C_g–Sm–N1 = 126.61(0), C_g–Sm–N2 = 126.72(0), C_g–Sm–C1 = 107.34(0), C_g–Sm–C1 = 107.74(0), N1–P1–C1 = 108.71(14), N2–P2–C1 = 109.13(13). **1c:** Yb–N1 = 2.353(3), Yb–N2 = 2.360(3), Yb–Cl = 2.5325(9), Yb–C1 = 2.594(3), Yb–C_g = 2.342(9), N1–P1 = 1.600(3), N2–P2 = 1.598(3), C1–P1 = 1.743(3), C1–P2 = 1.738(3); N1–Yb–N2 = 99.66(10), N1–Yb–Cl = 89.96(7), N2–Yb–Cl = 95.68(7), N1–Yb–C1 = 65.68(10), N2–Yb–C1 = 65.92(10), Cl–Yb–C1 = 144.74(7), C_g–Yb–N1 = 127.69(10), C_g–Yb–N2 = 126.13(10), C_g–Yb–Cl = 107.10(10), C_g–Yb–C1 = 108.05(10), N1–P1–C1 = 107.1(2), N2–P2–C1 = 108.1(2). C_g = C₅Me₅-ring centroid.

bond lengths to the cyclopentadienyl ring vary over the narrow range of 2.658(5)–2.679(5) Å (**1a**), 2.716(3)–2.732(3) Å (**1b**), and 2.618(4)–2.638(4) Å (**1c**). The Ln–Cl distances have the expected values of 2.5757(14) Å (**1a**), 2.6336(9) Å (**1b**), and 2.5325(9) Å (**1c**). The geometry of the very bulky {CH(PPh₂NSiMe₃)₂}[−] ligand is as expected.⁹ A six-membered metallacycle (N1–P1–C1–P2–N2–Ln) is formed by chelation of the two (trimethylsilyl)imine groups to the ytterbium atom. The ring adopts a twist-boat conformation, in which the central carbon atom and the rare earth atom are displaced from the N₂P₂ least-squares plane. The distances between the central carbon atom (C1) and the metal (2.649(4) Å (**1a**), 2.712(3) Å (**1b**), 2.594(3) Å (**1c**)) are longer than average Ln–C distances;¹⁴ however, a resultant tridentate coordination of the ligand is observed as before.⁹ The N1–Ln–N2 bite angle of the ligand (99.33(12)° (**1a**), 97.32(9)° (**1b**), and 99.66(10)° (**1c**)) depends, as expected, on the ion radius of the central metal.

Polymerization of ϵ -Caprolactone. So far, no rare earth halide compound, used as precatalyst for the polymerization of

ϵ -CL, has given spectacular results.^{15–17} Compounds **1a–c** by themselves only allowed the synthesis of poly(ϵ -CL) in low yields at ambient temperature within 90 min; however, the polymerization is not controlled (Tables 2–4, runs 1 and 2).

To explore the impact of compounds **1a–c** in ϵ -CL polymerization and to eventually detect new initiating systems, we directly investigated the reactivity of **1a–c** combined in situ with an alcoholic agent. Several authors have used various alcohols as a coinitiator for the solution polymerization of lactones and lactide from rare earth alkoxides or amides.^{6a,b,18,19} 2-Propanol, benzyl alcohol, and *tert*-butyl alcohol have been employed in excess (2–10 equiv) to generate in situ, upon alcohol–alkoxide exchange, an initiator less crowded/less aggregated than the original rare earth alkoxides Ln₅(μ -O)-(O*i*Pr)₁₃ or Ln(2,6-di-*tert*-butylphenolate).¹⁸ Poly(ϵ -CL) with $\bar{M}_n = 60\,000$ was prepared once in dichloromethane from a [ϵ -CL]₀/[*i*PrOH]₀/[Y(O(2,6-*t*-BuC₆H₃)₂)₃]₀ = 50/1/0.3 mixture in 5 min with complete conversion at 22 °C.^{18a} Aliphatic poly(ϵ -CL) was also prepared as a result of Y[N(SiMe₃)₂]₃/2-propanol exchange; chains of $\bar{M}_n = 20\,000$ were formed at complete monomer conversion within 3 min at 40 °C in toluene.^{19a} In the present work, we adapted this concept to an alcoholysis route from the organometallic chloride precursors **1a–c**. We thus found that addition of 2-propanol to **1a–c** provides an active initiator for ϵ -CL polymerization (Tables 2–4). Thus, to the best of our knowledge, this in situ alcoholysis of an organometallic chloride precursor is reported here for the first time for the direct elaboration of a rare earth alkoxide initiator that efficiently polymerizes a cyclic ester.

The in situ systems based on a 1:1 molar ratio of **1a–c** and HO*i*Pr exhibited a good efficiency toward ϵ -CL polymerization (Tables 2 and 3, runs 3–6; Table 4, runs 3–9). Under the same experimental conditions, these systems were clearly more active than those based on **1a–c** alone, respectively (Tables 2 and 3, run 4 vs runs 1 and 2; Table 4, runs 5 and 6 vs runs 1 and 2). Polymers synthesized from **1a,c** were obtained in quantitative yields within 90 min, and the molar masses were in quite good agreement with the calculated values. Using the samarium initiator, under the same experimental conditions as those used for the yttrium and ytterbium initiators ([**1**]₀ = 5.1 mmol.L^{−1}, reaction time 90 min), quantitative monomer conversion was not, however, reproducibly obtained. SEC curves always exhibited a unimodal, symmetric peak. With these **1a–c**/HO*i*Pr (1:1) systems, whatever the monomer to complex **1** ratio and the concentration in **1a–c** or ϵ -CL, a very narrow molar mass distribution was always obtained ($\bar{M}_w/\bar{M}_n < 1.20$; the average \bar{M}_w/\bar{M}_n value for all three complexes was 1.12). This observation

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Table 2. Polymerization of ϵ -CL Initiated by $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{Y}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}]$ (1a**) in THF at 23 °C**

run	[1a] ₀ (mmol L ⁻¹)	[ϵ -CL] ₀ (mmol L ⁻¹)	[ϵ -CL] ₀ /[1a] ₀	[HOiPr] ₀ /[1a] ₀	reacn time (min)	monomer conversn ^a (%)	$\bar{M}_n(\text{theor})$ g/mol ^b	$\bar{M}_n(\text{SEC})$ g/mol ^c	\bar{M}_w/\bar{M}_n^d
1	5.12	722	141	0	90	54	8 700	78 200	1.63
2	6.54	1128	172	0	45	10 ^e	<i>e</i>	<i>e</i>	<i>e</i>
3	5.12	410	80	1.0	90	100	9 200	9 300	1.11
4	5.15	716	141	1.0	90	100	16 100	12 100	1.11
5	5.22	1128	216	1.0	90	100	24 700	24 700	1.15
6	5.35	2255	422	1.0	90	100	48 200	38 700	1.20
7	5.13	410	80	1.5	90	100	6 100	7 500	1.18
8	5.36	722	135	1.5	90	100	10 300	14 400	1.13
9	5.13 ^f	1128	220	1.0	90	100	25 100	14 000	1.10
10	4.66 ^f	1845	396		90	100	45 200	22 800	1.15

^a Calculated from ¹H NMR analysis. ^b Calculated for one growing polymer chain per yttrium atom with $\bar{M}_n(\text{theor}) = ([\epsilon\text{-CL}]_0/[\text{HOiPr}]_0 \times 114 \times \text{conversion}) + 60$. ^c SEC values of precipitated polymer samples corrected with the coefficient 0.56. ^d Molar mass distribution calculated from SEC chromatogram traces. ^e Enough polymer could not be recovered for molar mass analysis. ^f Double monomer addition experiment.

Table 3. Polymerization of ϵ -CL Initiated by $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}]$ (1b**) in THF at 23 °C**

run	[1b] ₀	[ϵ -CL] ₀	[ϵ -CL] ₀ /[1b] ₀	[HOiPr] ₀ /[1b] ₀	reacn time (min)	monomer conversn ^a (%)	$\bar{M}_n(\text{theor})$ g/mol ^b	$\bar{M}_n(\text{SEC})$ g/mol ^c	\bar{M}_w/\bar{M}_n^d
1	5.12	722	141	0	90	22	3 600	160 000	1.40
2	5.11	867	170	0	45	10 ^e	<i>e</i>	<i>e</i>	<i>e</i>
3	5.12	410	79	1.0	90	100	9 100	9 000	1.14
4	5.12	722	140	1.0	90	100	16 050	16 200	1.14
5	5.06	1128	223	1.0	90	17	4 400	4 100	1.16
6	5.07	2200	434	1.0	90	20	10 000	9 300	1.13
7	5.21	410	79	1.5	90	23	2 100	3 100	1.15
8	5.25	694	132	1.5	90	24	3 600	4 600	1.13

^a Calculated from ¹H NMR analysis. ^b Calculated for one growing polymer chain per samarium atom with $\bar{M}_n(\text{theor}) = ([\epsilon\text{-CL}]_0/[\text{HOiPr}]_0 \times 114 \times \text{conversion}) + 60$. ^c SEC values of precipitated polymer samples corrected with the coefficient 0.56. ^d Molar mass distribution calculated from SEC chromatogram traces. ^e Enough polymer could not be recovered for molar mass analysis.

Table 4. Polymerization of ϵ -CL Initiated by $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}]$ (1c**) in THF at 23 °C ([ϵ -CL]₀ = 1128 mmol L⁻¹)**

run	[1c] ₀	[ϵ -CL] ₀ /[1c] ₀	[HOiPr] ₀ /[1c] ₀	reacn time (min)	monomer conversn ^a (%)	$\bar{M}_n(\text{theor})$ g/mol ^b	$\bar{M}_n(\text{SEC})$ g/mol ^c	\bar{M}_w/\bar{M}_n^d
1	5.21	139 ^e	0	90	18	2 900	27 100	1.45
2	5.10	221	0	45	12 ^e	<i>f</i>	<i>f</i>	<i>f</i>
3	14.18	80	1.0	45	100	9 200	9 300	1.12
4	7.98	141	1.0	45	90	14 500	15 600	1.08
5*	5.12	138	1.0	90	100	15 800	17 900	1.06
6	5.12	220	1.0	45	75	18 900	17 500	1.07
7	5.12	220	1.0	90	100	25 100	24 900	1.10
8	4.14	272	1.0	45	69	21 450	18 200	1.09
9*	5.18	436	1.0	90	100	49 800	45 500	1.14
10	13.77	82	1.5	45	100	6 300	6 800	1.11
11	11.16	101	1.5	45	98	7 500	8 500	1.12
12	8.31	136	1.5	45	95	9 900	10 400	1.09
13	6.04	187	1.5	45	93	13 300	12 800	1.09
14	5.15	219	3.0	45	80	6 700	8 500	1.10
15	5.40	209	15.0	45	96	1 600	3 100	1.16
16	5.21 ^g	217	1.0	45	75	18 600	17 300	1.06
17	2.89 ^g	446		90	88	44 800	33 100	1.08

^a Calculated from ¹H NMR analysis. ^b Calculated for one growing polymer chain per ytterbium atom with $\bar{M}_n(\text{theor}) = ([\epsilon\text{-CL}]_0/[\text{HOiPr}]_0 \times 114 \times \text{conversion}) + 60$. ^c SEC values of precipitated polymer samples corrected with the coefficient 0.56. ^d Molar mass distribution calculated from SEC chromatogram traces. ^e [ϵ -CL]₀ = 722 mmol L⁻¹. ^f Enough polymer could not be recovered for molar mass analysis. ^g Double monomer addition experiment. * [ϵ -CL]₀ = 705 (run 5); 2256 (run 9) mmol·L⁻¹.

is consistent with the quasi-absence of transesterification reactions all along the propagation step. These results, along with the number of active sites per metal ($\bar{M}_n(\text{theor})/\bar{M}_n(\text{SEC})$), which is close to unity, are in agreement with the generation of only one type of active species upon the stoichiometric alcoholysis with 2-propanol. In addition to the sometimes partial conversions obtained with **1b**, the nature of the metal does not seem to significantly influence these results. For \bar{M}_w/\bar{M}_n , the smallest ytterbium ($\bar{M}_w/\bar{M}_n < 1.14$; average $\bar{M}_w/\bar{M}_n = 1.09$) and yttrium ($\bar{M}_w/\bar{M}_n < 1.20$; average $\bar{M}_w/\bar{M}_n = 1.14$) complexes

displayed better values compared to the larger samarium ($\bar{M}_w/\bar{M}_n < 1.16$; average $\bar{M}_w/\bar{M}_n = 1.14$).²⁰ Addition of an equimolar amount of 2-propanol to **1a–c** thus allowed the polymerization to be controlled, at least within the time required for complete monomer conversion.

Addition of an excess of HOiPr ($n > 1$, $n = 1.5, 3, 15$ equiv vs $n = 1$ equiv; Tables 2 and 3, runs 7 and 8; Table 4, runs 10–15) resulted in measured molar mass values higher than

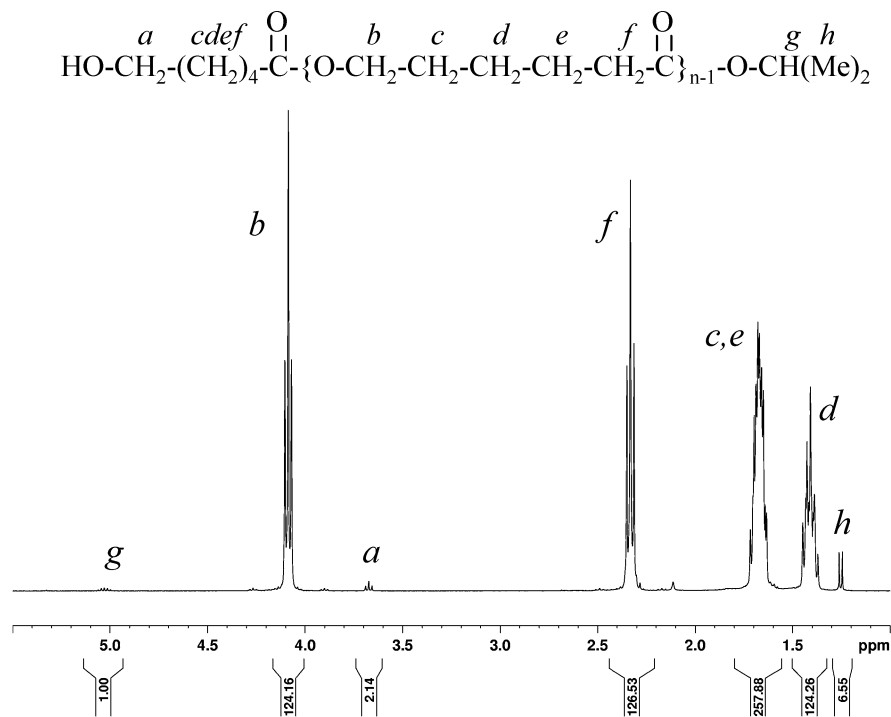


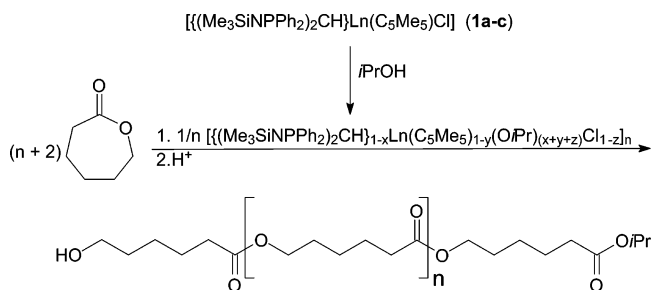
Figure 2. ^1H NMR spectrum in CDCl_3 of $\text{HO}(\text{CH}_2)_5\text{C}(\text{O})\{\text{O}(\text{CH}_2)_5\text{C}(\text{O})\}_{78}\text{O}(\text{CH}_2)_6\text{OiPr}$ prepared through ring-opening polymerization of $\epsilon\text{-CL}$ initiated by **1a** in THF with $[\epsilon\text{-CL}]_0 = 410 \text{ mmol L}^{-1}$ and $[\epsilon\text{-CL}]_0/3[\mathbf{1a}]_0 = 5.13 \text{ mmol L}^{-1}$ ($\bar{M}_n(\text{NMR}) = 7100$).

those calculated with subsequently less than one active chain per metal. The number of active chains per ytterbium was close to unity (0.95) for $n = 1.5$ and much lower than 1 (0.66) for $n = 3, 5$ (Table 4, runs 10–15). In addition, the greater the alcohol content in the reaction medium, the larger the observed difference between \bar{M} (theor) and \bar{M}_n (SEC) (Table 4, runs 6–14). For all polymers, the molar mass distribution remained below 1.20. These features most likely result from the presence of more than one initiating species when the value of n exceeds 1. Such an effect of excess alcohol on the polymer features has already been observed previously (at 10–18 equiv of added alcohol) and most likely reflects the role of added alcohol as chain transfer agent, resulting in active species of various structures.^{18c,19}

Evidence of the pseudo-living character of the **1a**–*c*/HO*iPr* (1:1) initiating systems is provided by the successful double monomer addition experiments (Table 2, runs 9 and 10; Table 4, runs 16 and 17). The size exclusion chromatogram exhibiting a symmetrical peak at the end of the first monomer feed showed a peak completely shifted toward higher \bar{M}_n as a result of polymerization resumption, while the molar mass distribution remained narrow (<1.15). This then initiates the route to the synthesis of block polymers.^{18a,19}

The polymers recovered after hydrolysis and precipitation in cold pentane were unambiguously shown by ^1H NMR analysis to be systematically capped by a caproyl hydroxyl group at one end and an isopropyl ester group at the second extremity (Figure 2). This was unequivocally confirmed by MALDI-TOF analysis, which indeed exhibited only one kind of macromolecule capped by hydroxyl and alkoxide end groups. The NMR spectra were identical with those previously recorded for $\text{HO}-\text{P}(\epsilon\text{-CL})-\text{OiPr}$ synthesized from “ $\text{Ln}(\text{OiPr})_3$ ”.^{19,21} These specific $\text{HO}-\text{CH}_2$ and $\text{C}(\text{O})-\text{iPr}$ chain ends resulted from the deactivation of a rare earth alkoxide growing species and from the presence in the initial initiating system of a $\text{Ln}-\text{OiPr}$ bond within which the monomer was polymerized, respectively. The number-average

Scheme 2. Proposed Mechanism for the Synthesis of α -Hydroxy, ω -Alkoxy Telechelic Poly(ϵ -caprolactone)



molar mass of short-length P(ϵ -CL) chains (for instance Table 4, run 3) calculated from the ^1H NMR spectrum ($\bar{M}_n(\text{NMR}) = 8900$), i.e. from the relative intensities of the methylene protons of the polymer chains ($\text{CH}_2\text{OC}(\text{O})$) and from the protons of the end groups (either the isopropoxy ester or the hydroxy methylene), was in good agreement with $\bar{M}_n(\text{theor}) (=9200)$ and $\bar{M}_n(\text{SEC}) (=9300)$. This confirmed that the chain end capping was quantitative at both ends. Obviously, some exchange process of a coordinated ligand of **1a-c** with free 2-propanol is involved.

For mechanistic investigations we reacted on an NMR scale the samarium compound **1b** with HO*iPr*. In the ^1H NMR spectra it is clearly seen that, with an excess of HO*iPr* complex, **1b** totally decomposes but no precipitate is observed. By using 1 equiv of HO*iPr* or less, we observe that the $\eta^5\text{-C}_5\text{Me}_5$ ring and also the $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}^-$ ligand are equally yet not fully protonated and thus are substituted to some extent by $-\text{OiPr}$. Since NMR analysis cannot show a potential chloride exchange, this cannot be ruled out either. Thus, alcoholysis of the organometallic chloride precursors **1a-c** is most likely a very complicated protonation process resulting in some mixed active alkoxide species, as depicted in Scheme 2. The very narrow molar mass distributions obtained, most likely resulting from the stereoelectronic demand and/or constraint of the ancillary (phosphinimino)methanide ligand, suggest that this one ligand

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remains coordinated, to some extent, to the metal center. As shown by the polymer analysis, the monomer inserts into the Ln–OiPr bond for the polymerization reaction to proceed. Similar observations were recently made by Yao and Shen.²² Some oligomeric alkoxide species already reported in the literature are most likely formed upon concentration.²³ Attempts to isolate the proposed alkoxide active compound on a preparative scale did not lead to a well-defined species.

Conclusion

In summary, a series of pentamethylcyclopentadienyl bis-(phosphinimino)methanide complexes of yttrium and the lanthanides, $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}]$ (Ln = Y, Sm, Yb), were prepared by two different synthetic approaches. The title compounds can be obtained either from $[\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{LnCl}_2]_2$ and $\text{K}(\text{C}_5\text{Me}_5)$ or in a one-pot reaction, when $\text{K}\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}$ and $\text{K}(\text{C}_5\text{Me}_5)$ are reacted with anhy-

drous yttrium or lanthanide trichlorides in a 1:1:1 molar ratio in THF. Combination of **1a–c** with a stoichiometric amount of HOiPr (1 equiv) successfully led to highly efficient systems for the controlled ROP of ϵ -CL. The resulting active $[\text{Ln}]\text{-OiPr}$ initiator exhibited a reactivity similar to that of well-defined rare earth alkoxide complexes offering very narrow molar mass distributions, especially with ytterbium. The most noticeable and striking results of this preliminary screening is that an active alkoxide initiator is formed in situ from an organometallic chloride precursor. This is indeed the first example so far of addition of an alcohol to a non-alkoxide or non-amide precursor. This initiating system is also versatile, since when the alcohol type is changed, a wide range of asymmetric telechelic polymers should be obtained straightforwardly. Such a direct and handy route to active rare earth initiating complexes from the synthetically more accessible halogen analogues is intended to be widely applied to the generation of a large variety of initiators.

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Supporting Information Available: CIF files giving crystallographic data for **1a–c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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