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Rare-Earth Amidate Complexes. Easily Accessed Initiators For ε-Caprolactone Ring-Opening Polymerization

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The direct synthesis of yttrium amidate complexes using the simple reaction of amide proligands and $Y(N(SiMe_3)_2)_3$ results in the high-yielding preparation and isolation of crystalline, monomeric materials. The complex, tris(*N*-2′,6′-diisopropylphenyl(naphthyl)amidate)yttrium mono(tetrahydrofuran) (**4**), was structurally determined to be a 7-coordinate C_1 symmetric structure, maintaining one bound tetrahydrofuran molecule. Compound **4** ($C_{12}H_{17}[NCO]C_{10}H_7)_3Y(C_4H_8O$) crystallized in the monoclinic space group $P2(1)/c$ with $a = 13.7820(11)$ Å, $b = 33.598(3)$ Å, $c = 16.0575(12)$ Å, $\alpha = 90°$, $\beta = 98.762(3)°$, $\gamma = 90°$, $Z = 4$. Solution phase NMR spectroscopic characterization of this same complex showed a highly symmetric species, consistent with a fluxional coordination environment for these compounds. Preliminary studies into the initiation of ε-caprolactone ring-opening polymerization using these complexes indicate high activity, producing high molecular weight polymer.

Introduction

Rare-earth complexes are very attractive catalyst systems because of their low toxicity, low cost, and high reactivity.[1−13] Easily accessed and modular ligand sets suitable for rare-earth complexation are ideally suited for the optimization of catalytic activity for these compounds. To this end, substantial research with group 3 and lanthanide complexes containing ancillary nitrogen donor ligands such as amido,[1−3,14−23] amido pyridinate,[24] amidinate,[4,25−27] guanidinate,[5,6,28−37] and β-diketiminate[7−12,38−43] ligand sets has been conducted. However, the synthesis of discrete rare-earth

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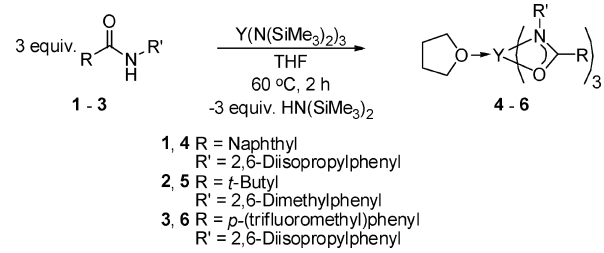
complexes as catalyst precursors can be difficult because of low energy ligand redistribution pathways. Furthermore, because of the high Lewis acidity of these rare-earth metals, in combination with their larger radii, synthetic approaches using multidentate ligands often results in dimer formation or even higher aggregates.[44] Typically, the formation of discrete species is most commonly controlled by the steric environment of the ligand. Furthermore, facile modification of steric and electronic properties of the ancillary ligand of new complexes is desirable for catalyst optimization. To this end, homoleptic amidinate complexes of the lanthanides and group 3 metals have been extensively investigated and have been modestly successful in ring-opening polymerization of ε-caprolactone.[45,46] However, the similar ancillary amidate ligand, which replaces one nitrogen donor for an oxygen donor, has been largely overlooked as a class of auxiliary ligand capable of providing variable reactivity at the metal center in the resultant complexes. Our research focuses on new high-yielding preparative methods to access crystalline, discrete rare-earth amidate complexes that display promising catalytic activity. Here we report a direct route for the synthesis, isolation, and characterization of a family of crystalline, yttrium tris(amidate) complexes which rapidly initiate the ring-opening polymerization of ε-caprolactone to give high molecular weight, biodegradable, polyester product.

Recently our research group has demonstrated that bis(amidate)bis(amido) complexes of group 4 metals are tunable catalysts for the hydroamination of alkynes,[47,48] alkenes,[49,50] and allenes.[51] The amide proligands can be easily varied for desired steric and electronic properties because of their facile synthesis, from acid chlorides and primary amines. The resultant organic amides can be used in the direct preparation of homoleptic group 3 amidate complexes with a protonolysis reaction of organic amides with commercially available $Y(N(SiMe_3)_2)_3$ (Scheme 1) to give easily purified crystalline materials. This contrasts with previous examples of amidate complexes of the lanthanide and group 3 metals that have been synthesized via isocyanate insertion into a reactive M−C bond of lanthanide alkyl complexes.[52−54] This preparative approach typically yields amidate bridged bimetallic complexes, which can be fully characterized.[53] Moreover, a decomposition product of an attempted isocyanate insertion reaction led to the only previous report of a homoleptic lanthanide amidate complex,[53] a $Ho[OC(Bu^n)NPh]_3$ complex, which was characterized by elemental analysis and IR spectroscopy but no structural information was provided.[53] While the isocyanate insertion method is well established, the requisite lanthanide alkyl starting materials are nontrivial to synthesize and handle. Furthermore, this route has been exploited for the exploration of the reactivity of M−C bonds, rather than using the resultant amidate complexes as potential tunable catalytic systems. Most importantly, our direct, high-yielding route gives easily isolable monomeric, crystalline amidate complexes that show promising reactivity in the ring-opening polymerization of lactones.

Scheme 1. Synthesis of Tris(amidate) Complexes



Experimental Section

All operations were performed under an inert atmosphere of nitrogen using standard Schlenk-line or glovebox techniques. Tetrahydrofuran (THF), toluene, pentane, and hexanes were all purified by passage through an alumina column and sparged with nitrogen. ε-Caprolactone was dried by stirring over CaH_2 for 4 days, allowed to settle for 2 days, decanted to a new flask and then distilled under reduced pressure, and stored over molecular sieves. $Y(N(SiMe_3)_2)_3$ was synthesized as described in literature.[55] All other

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chemicals were commercially available and used as received unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV300, AV400, and AV600 spectrometers. Molecular weights were estimated by triple detection gel permeation chromatography (GPC - LLS) using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6 × 300 mm) HR5E, HR4 and HR2, Waters 2410 differential refractometer, Wyatt tristar miniDAWN (laser light scattering detector), and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL min^{-1} was used and samples were dissolved in THF (ca. 4 mg mL^{-1}). Molecular weights were determined by comparison to a polystyrene standard curve, and absolute molecular weights were determined using a dn/dc of 0.079 mL g^{-1}.[56,57] Elemental analyses and mass spectra were performed by the microanalytical laboratory of the Department of Chemistry at the University of British Columbia. X-ray crystallography was conducted at the University of British Columbia by Dr. Brian Patrick. Structure **4** was modified using the squeeze function of the Platon software package to remove disordered THF.[58] Compounds **1** and **2** have been previously reported, but complete characterization data was not provided.[59−62]

Synthesis of *N*-(Diisopropylphenyl)naphthyl Amide (1). To a 250 mL round-bottom flask was added 2,6-diisopropylaniline (4.95 mL, 26.2 mmol) dissolved in 125 mL of dichloromethane. The reaction mixture was cooled to 0 °C, and triethylamine (8 mL) was added dropwise by syringe. The resulting solution was stirred for 5 min with subsequent dropwise addition of 1-naphthoyl chloride (3.95 mL, 26.2 mmol). The reaction was stirred overnight and then was washed with 1 M HCl (3 × 50 mL), followed by 1 M NaOH (30 mL), and brine (30 mL). The organic layer was dried over $MgSO_4$, filtered, then concentrated under reduced pressure to obtain a beige solid. The solid was recrystallized twice from hot toluene to obtain a white powder. Yield: 7.94 g, 91%. ^{1}H NMR ($CDCl_3$, 300 MHz, 293 K) δ 8.46 (d, ^3J = 6 Hz, 1H, 9-naphthyl-*H*), 7.98 (d, ^3J = 6 Hz, 1H, 6-naphthyl-*H*), 7.90 (d, ^3J = 6 Hz, 1H, 4-naphthyl-*H*), 7.83 (d, ^3J = 5 Hz, 1H, 2-naphthyl-*H*), 7.57 (m, 3H, 8,7,3-naphthyl-*H*), 7.36 (t, ^3J = 6 Hz, 1H, 4-diisopropylphenyl-*H*), 7.25 (d, ^3J = 6 Hz, 2H, 3,5-diisopropylphenyl-*H*), 7.21 (s, 1H, N-*H*), 3.30 (septet, ^3J = 5 Hz, 2H, C*H*(CH_3)$_2$), 1.28 (d, ^3J = 5 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 293K) δ 170.4 (*C*═O), 147.8, 135.6, 135.3, 132.5, 132.2, 131.9, 130.1, 129.8, 128.8, 128.0, 126.8, 126.2, 126.1, 125.0 (aryl *C*), 30.4 (*C*H(CH_3)$_2$), 25.2(CH(*CH*$_3$)$_2$). IR data (KBr, cm^{-1}): 3253 (br), 3047 (w), 2961 (s), 2865 (w), 1643 (s), 1591 (w), 1517 (s), 1297 (w), 913 (w), 785 (w), 734 (w), 654 (w). EIMS(*m*/*z*): 331 [M]$^+$. Anal. Found (calcd for $C_{23}H_{25}NO$): C 83.74% (83.34%), N 4.55% (4.23%), H 7.54% (7.60%).

Synthesis of *N*-(2,6-Dimethylphenyl)*t*-butyl Amide (2). The experimental method described for **1** was used in the preparation of **2** using 2,6-dimethylaniline (5.10 mL, 0.041 mol) and trimethylacetyl chloride (5.05 mL, 0.041 mol). Yield: 7.07 g, 84%. ^{1}H NMR (C_6D_6, 400 MHz, 293 K) δ 7.05 (m, 1H, phenyl-*H*), 6.95 (m, 2H, phenyl-*H*), 6.17 (s, 1H, N-*H*), 2.09 (s, 6H, C*H*$_3$), 1.08 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz, 293 K) δ 175.6 (*C*═O), 135.6, 135.1, 127.7, 126.6 (phenyl *C*), 38.7 (*C*(CH_3)$_3$), 27.3 (C(*CH*$_3$)$_3$), 18.0 (*CH*$_3$). IR data (KBr, cm^{-1}): 3295 (br), 3021 (w), 2956 (s), 2921 (w), 1650 (s), 1593 (w), 1506 (s), 1278 (w), 1221 (m) 938 (w), 768 (s), 722 (w), 647 (w). EIMS(*m*/*z*): 205 [M]$^+$. Anal. Found (calcd for $C_{13}H_{19}NO$): C 76.12% (76.06%), N 7.00% (6.82%), H 9.09% (9.33%).

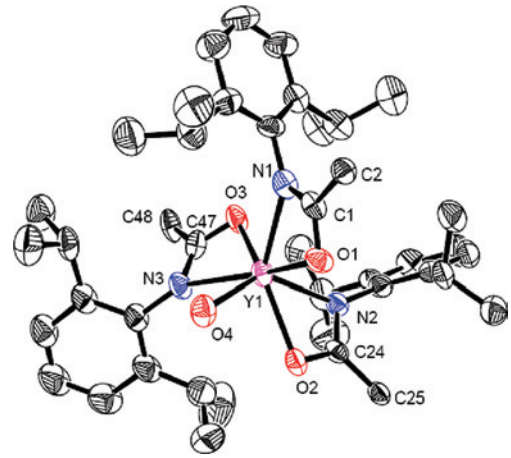

Figure 1. Oak Ridge Thermal Ellipsoid Plot (ORTEP) diagram of the solid-state molecular structure of [(THF)Y(Nap[O,N](i-Pr)$_2$Ph)$_3$]$_2$ (**4**) with the probability ellipsoids drawn at the 50% level. Naphthyl groups (except for *ipso*-carbon) and the carbons of the THF groups omitted for clarity.[65]

Synthesis of *N*-(2,6-Diisopropylphenyl)*p*-(trifluoromethyl)phenyl Amide (3). The experimental method described for **1** was used in the preparation of **3** using 2,6-diisopropylaniline (6.30 mL, 33.4 mmol) and *p*-(trifluoromethyl)benzoyl chloride (5.00 mL, 33.6 mmol). Yield: 9.24 g, 79%. ^{1}H NMR (C_6D_6, 600 MHz, 293 K) δ 7.47 (d, ^3J = 12 Hz, 2H, aryl-*H*), 7.25 (m, 2H, aryl-*H*), 7.14 (m, 3H, aryl-*H*), 6.68 (s, 1H, N-*H*), 3.08 (septet, ^3J = 6 Hz, 2H, C*H*(CH_3)$_2$), 1.21 (d, ^3J = 6 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 375 MHz, 293K) δ 164.1 (*C*═O), 146.10, 137.2, 132.5, 130.8, 128.3, 125.1, 123.2 (aryl *C*), 28.6 (*C*H(CH_3)$_2$), 23.2 (CH-(*C*H$_3$)$_2$). IR data (KBr, cm^{-1}): 3300 (br), 2966 (s), 2929 (s) 1648 (s), 1580 (w), 1530 (s), 1500 (s), 1330 (m), 1317 (w), 1158 (w), 1116 (w), 862 (w), 801 (w). EIMS(*m*/*z*): 349 [M]$^+$. Anal. found (calcd for $C_{20}H_{22}F_3NO$): C 68.75% (68.75%), N 4.30% (4.01%), H 6.64% (6.35%).

Synthesis of Tris(*N*-2′, 6′-diisopropylphenyl(naphthyl)amidate)yttrium Mono(tetrahydrofuran) (4). Inside a nitrogen filled glovebox, a vial was charged with amide **1** (0.205 g, 0.618 mmol), yttrium tris(bis(trimethylsilyl)amide) (0.118 g, 0.206 mmol), and a stirbar. To this, 5 mL of tetrahydrofuran was transferred to the reaction vessel at room temperature. The solution was stirred within the glovebox for 2 h at 60 °C, and then filtered through Celite and concentrated under reduced pressure to a pale yellow powder. The product was recrystallized by dissolving in a minimum amount of hexanes and then left at −30 °C to yield colorless crystals. Yield: 0.223 g, 94%. X-ray quality crystals were grown from cold hexanes. Refer to Figure 1, and Table 1 for crystallographic data. ^{1}H NMR (300 MHz, C_6D_6) δ 9.43 (d, J = 9 Hz, 3H, aryl-*H*), 7.70 (d, J = 8 Hz, 3H, aryl-*H*), 7.66−7.60 (m, 10H, aryl-*H*), 7.55 (d, J = 8 Hz, 3H, aryl-*H*), 7.43 (t, J = 8 Hz, 3H, aryl-*H*), 7.33 (s, 5H, aryl-*H*), 7.02 (t, J = 7 Hz, 3H, aryl-*H*), 4.25 (broad m, 4H, O−C*H*$_2$), 3.90 (septet, J = 7 Hz, 6H, C*H*(CH_3)$_2$), 1.58 (m, 4H, O-CH$_2$C*H*$_2$), 1.21 (d, J = 7 Hz, 18H, CH(C*H*$_3$)$_2$), 0.94 (d, J = 7 Hz, 18H, CH(C*H*$_3$)$_2$). ^{13}C NMR (100.6 MHz, C_6D_6) δ 180.1 (*C*═O), 142.3, 141.6, 134.3,

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Table 1. Crystallographic Data and Structure Refinement Details for **4**

empirical formula	$C_{73}H_{80}N_3O_4Y$
f_w	1152.31
temperature (K)	173(2)
wavelength (Å)	0.71073
cryst. syst., space group	monoclinic, *P*2(1)/*c*
unit cell dimensions	
a, *b*, *c* (Å)	13.7820(11), 33.598(3), 16.0575(12)
α, *β*, *γ* (deg)	90, 98.762(3), 90
volume (Å^3), *Z*	7348.7(10), 4
calcd. density (g/cm^3)	1.042
abs. coeff (mm^{-1})	0.837
F(000)	2440
cryst. size (mm)	0.25 × 0.20 × 0.20
data collection *θ* range (deg)	1.77−22.77
limiting indices	$-12 \le h \le 14$, $-36 \le k \le 36$, $-17 \le l \le 16$
reflections collected	43713
indep. reflections	9816 [*R*(int) = 0.0735]
completeness to *θ* = 22.77° (%)	98.8
abs. correction	semiempirical from equivalents
max and min transmn	0.846 and 0.515
refinement method	Full-matrix least-squares on F^2
data/restraints/param	9816/0/744
GOF on F^2	0.976
final R indices [$I > 2\sigma(I)$]	R1 = 0.0614, wR2 = 0.1492
R indices (all data)	R1 = 0.1040, wR2 = 0.1649
largest diff. peak and hole (e/Å^3)	0.590 and −1.863

132.1, 132.0, 130.1, 129.4, 128.3, 127.8, 127.5, 127.4, 127.3, 126.3, 125.4, 124.3, 123.9, 123.6, 123.5 (aryl-*C*), 69.6 (O-*C*H$_2$), 28.1 (O-CH$_2$*C*H$_2$), 25.0 (*C*H(CH$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$). IR (KBr, cm^{-1}): 3052 (w), 2960 (s), 2860 (w), 1573 (w), 1513 (vs), 1406 (vs), 1382 (vs), 1318 (w), 1251 (s), 1191 (s), 1024 (s), 915 (s), 840 (w), 800 (w), 779 (s), 761 (w), 657 (w), 621 (w), 564 (w), 506 (w), 459 (w) cm^{-1}. MS (EI): 1079 (M$^+$), 952 (M$^+$ − Nap), 749 (M$^+$ − Nap[O,N]Dipp), 331 (M$^+$ − Y(Nap[O,N]Dipp)$_2$). Anal. found (calcd. for $C_{73}H_{80}N_3O_4Y$): C 75.70% (76.09%), H 6.61% (7.00%), N 3.68% (3.65%).

Synthesis of Tris(*N*-2′, 6′-dimethylphenyl(tert-butyl)amidate)yttrium Mono(tetrahydrofuran) (5). The experimental method described for **4** was used in the preparation of **5** using **2** (0.201 g, 0.981 mmol) and yttrium tris(bis(trimethylsilyl)amide) (0.187 g, 0.327 mmol) to give a yellow oil which solidified over time. The product was recrystallized by dissolving in a minimum amount of hexanes and then left at −30 °C to give a white crystalline solid. Yield: 0.223 g, 88%. ^{1}H NMR (300 MHz, C_6D_6) *δ* 6.88 (m, 9H, aryl-*H*), 3.67 (m, 4H, O-C*H*$_2$), 2.24 (s, 18H, C*H*$_3$), 1.28 (m, 4H, O-CH$_2$C*H*$_2$), 1.08 (s, 27H, C(C*H*$_3$)$_3$). ^{13}C NMR (100.6 MHz, C_6D_6) *δ* 185.2 (*C*═O), 145.8, 130.8, 127.4, 122.7 (aryl-*C*), 68.7 (O-*C*H$_2$), 41.2 (O-CH$_2$*C*H$_2$), 28.0 (*C*(CH$_3$)$_3$), 25.0 (*C*H$_3$), 19.2 (*C*H$_3$). IR (KBr, cm^{-1}): 2986 (w), 2951 (s), 2904 (w), 1541 (s), 1522 (s), 1477 (s), 1398 (s), 1352 (w), 1219 (s), 1183 (s), 927 (s), 759 (s), 605 (w) cm^{-1}. MS (EI): 701 (M$^+$), 686 (M$^+$ − CH$_3$), 644 (M$^+$ − *t*Bu), 497 (M$^+$ − (*t*Bu[O,N]Dmp). Anal. found (calcd for $C_{43}H_{62}N_3O_4Y$): C 66.70% (66.74%), N 6.25% (5.43%), H 7.89% (8.08%).

Synthesis of Tris(*N*-2′, 6′-diisopropylphenyl(*p*-(trifluoromethylphenyl)amidate)yttrium Mono(tetrahydrofuran) (6). The experimental method described for **4** was used in the preparation of **6** with amide **3** (0.401 g, 1.15 mmol) and yttrium tris(bis(trimethylsilyl)amide) (0.220 g, 0.386 mmol) to give a yellow oil which solidified over time. The product was recrystallized by dissolving in a minimum amount of hexanes and then left at −30 °C to give a white crystalline solid. Yield: 0.365 g, 79%. ^{1}H NMR (400 MHz, C_6D_6) *δ* 7.65 (d, *J* = 8 Hz, 6H, aryl-*H*), 7.20 (m, 6H, aryl-*H*), 7.12 (m, 9H, aryl-*H*), 3.89 (m, 4H, O−C*H*$_2$), 3.46 (septet, 6H, *J* = 7 Hz, C*H*(CH$_3$)$_2$), 1.41 (m, 4H, O-CH$_2$C*H*$_2$), 1.12 (d, 18H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 0.89 (d, 18H, *J* = 7 Hz, CH(C*H*$_3$)$_2$). ^{13}C NMR (100.6 MHz, C_6D_6) *δ* 175.7, 142.5, 141.2, 137.6, 132.4 (q, *J* = 32 Hz, *C*F$_3$), 130.5, 125.4, 124.7, 124.3 (aryl-*C*), 71.5 (O-*C*H$_2$), 28.5 (*C*H(CH$_3$)$_2$), 25.4 (O-CH$_2$*C*H$_2$), 24.6 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$). IR (KBr, cm^{-1}): 2964 (w), 1617 (s), 1528 (s), 1503 (s), 1409 (s), 1325 (s), 1167 (w), 1129 (s), 1066 (s), 925 (w), 858 (s), 764 (w), 697 (w) cm^{-1}. MS (EI): 1133 (M$^+$), 785 (M$^+$ − *p*-CF$_3$phenyl-[O,N]Dipp), 349 (*p*-CF$_3$phenyl[O,N]Dipp). Anal. found (calcd for $C_{64}H_{71}F_9N_3O_4Y$): C 62.36% (63.73%), N 3.43% (3.48%), H 6.16% (5.93%).

General Procedure for *ε*-Caprolactone Ring-Opening Polymerization (225:1 Monomer to Initiator Ratio). Inside a nitrogen filled glovebox, complex **4** (13.5 mg, 0.0117 mmol) was dissolved in 5 mL of toluene. The colorless solution was transferred to a 10 mL vial, equipped with a stir bar. *ε*-Caprolactone (0.3008 g, 2.64 mmol) was dissolved in 5 mL of toluene and pipetted directly into the vigorously stirring solution of complex **4**. The reaction was stirred for 15 min within the glovebox and then exposed to air. A couple drops of 1 M HCl solution was added to fully quench. The polymer was precipitated from cold petroleum ether. The polymer was isolated by vacuum filtration, and then dried overnight in vacuo. Yield: 0.270 g, 90%.

Results and Discussion

Homoleptic yttrium complexes can be made from proligands **1** (*N*-(diisopropylphenyl) naphthyl amide), **2** (*N*-(dimethylphenyl) *t*-butyl amide) and **3** (*N*-(diisopropylphenyl) *p*-(trifluoromethyl)phenyl amide) using a simple protonolysis reaction. The complexes formed (**4**, **5**, and **6**) were recrystallized from hexanes to give colorless crystals in high yield (94% for **4**, 88% for **5**, and 79% for **6**). These air and moisture sensitive complexes were fully characterized and are soluble in all common hydrocarbon solvents.

The ^{1}H NMR spectra of complexes **4**, **5**, and **6** have very similar characteristics, and all spectra show C_3 symmetric structures in the solution phase and contain 1 equiv of THF. In complexes **4** and **5**, the signals observed for the THF methylene protons are shifted (*δ* 4.25 ppm and 1.58 ppm for **4**, *δ* 3.89 ppm and 1.42 ppm for **5**) and broadened from typical residual THF solvent signals (*δ* 3.57 ppm and 1.40 ppm).[63] This data is consistent with labile, coordinated THF that is rapidly exchanging on the NMR time scale. Variable temperature NMR spectroscopic experiments on complex **4** failed to yield any energetic parameters for this exchange, as no line-broadening was observed down to −45 °C. Furthermore, the overall C_3 symmetry of this complex was maintained at these lower temperatures, also with no observable line broadening, consistent with either a highly fluxional complex or a static structure. ^{1}H NMR spectrum of complex **5** shows THF methylene proton signals even after exposure of the complex to vacuum overnight at 25 °C, but after exhaustive pumping (more than 3 days) the THF can be partially removed. However, this is not the case for complexes **4** and **6**, as exhaustive vacuum does not remove the THF molecule.

IR spectroscopy is very diagnostic for the formation of these complexes as the disappearance of the N−H stretch from proligands and a shift of the C═O stretches are consistently observed. For example, from proligand **1** to the formation of complex **4**, the disappearance of the N−H

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex **4**

	bond length (Å) or bond angle (deg)		bond length (Å) or bond angle (deg)
Y1−O1	2.334(3)	Y1−O1−C1	95.8(3)
Y1−N1	2.386(4)	O1−C1−N1	115.5(4)
O1−C1	1.292(5)	C1−N1−Y1	93.0(3)
N1−C1	1.304(5)	N1−Y1−O1	55.44(12)
Y1−O2	2.307(3)	Y1−O2−C24	94.8(3)
Y1−N2	2.369(3)	O2−C24−N2	117.0(4)
O2−C24	1.272(5)	C24−N2−Y1	90.8(3)
N2−C24	1.318(5)	N2−Y1−O2	56.38(11)
Y1−O3	2.268(3)	Y1−O3−C47	97.6(3)
Y1−N3	2.479(4)	O3−C47−N3	118.5(4)
O3−C47	1.293(6)	C47−N3−Y1	87.8(3)
N3−C47	1.304(6)	N3−Y1−O3	55.87(12)
Y1−O4	2.332(3)		

stretch (3253 cm^{-1} for **1**) and the shifting of the C═O stretch from 1643 cm^{-1} to 1513 cm^{-1} is observed. This weakening of the C═O stretch is consistent with both amidate delocalization and metal complexation. Furthermore, the appearance of a weak C═N stretch at 1406 cm^{-1} supports the formation of the desired complex with the delocalized monoanionic ligand. These IR trends are mirrored in complexes **5** and **6** (C═O stretch: 1650 cm^{-1} to 1541 cm^{-1} for **2** to **5** and 1648 cm^{-1} to 1528 cm^{-1} for **3** to **6**). Finally, mass spectrometry of **4**, **5**, and **6** gives molecular ion peaks corresponding to the complex without THF in all cases, and the fragmentation pattern for these complexes show signals for the loss of one ligand and for the free ligand itself.

X-ray quality crystals of complex **4** can be grown from hexanes at −35 °C, and the solid-state molecular structure is shown in Figure 1. The 7-coordinate C_1 symmetric molecular structure of **4** confirms electron delocalization through the κ^2-amidate backbone as indicated by the C−O and C−N bond lengths (average C−O is 1.290 Å and average C−N is 1.310 Å). The average sum total of the four angles of each amidate metallacycle is 359.5°, indicating no significant deviation from planarity (see Table 2). This is similar to a previously reported product from an isocyanate insertion reaction, in which a related monoamidate yttrium complex, $(MeC_5H_4)_2Y(THF)(N(^iPr)_2[O,N]Ph)$, has a similar Y−O(amidate) bond at 2.285(2) Å.[64]

In contrast, initial preparative efforts toward yttrium amidate complexes using salt metathesis illustrated the propensity for amidate ligands to promote the formation of bridged dimeric or ill-defined multimetallic species. The use of traditional salt metathesis routes typically resulted in the formation of insoluble, ill-defined "ate" complexes. However, the amidate salt of *N*-2′,6′-dimethylphenyl(*t*-butyl)amide (**2**) could be formed in situ by addition of an equivalent of sodium bis(trimethylsilyl)amide suspended in THF, and after solvent removal, the amidate salt was reacted directly with yttrium trichloride, in a 3:1 molar ratio. The product was recrystallized from warm toluene to give dinuclear complex **7** in low yield. Unfortunately full characterization was not possible as this low yielding crystalline sample was not representative of the bulk material which had complex NMR spectra consistent with a highly fluxional species of ill-defined structure in the solution phase. Notably, the use of the large sodium counterion and bulky base were found to be necessary as deprotonation of **2** with *n*-butyllithium and subsequent reaction with yttrium trichloride resulted in the formation of completely insoluble materials.

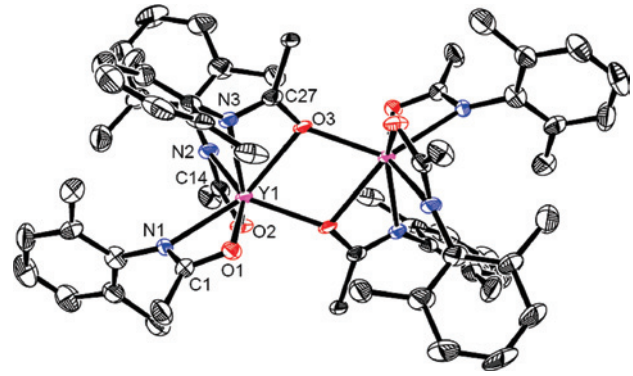


Figure 2. ORTEP of $[Y(tBu[O,N](CH_3)_2Ph)_3]_2$ (**7**) with the probability ellipsoids drawn at the 50% level. *t*Bu groups omitted for clarity.[66] Selected bond lengths (Å) and bond angles (deg): Y1−O1 2.260(4), Y1−N1 2.449(5), O1−C1 1.286(8), N1−C1 1.299(9), Y1−O2 2.270(4), Y1−N2 2.492(5), O2−C14 1.286(8), N2−C14 1.309(9), Y1−O3 2.384(4), Y1−N3 2.483(5), O3−C27 1.327(8), N3−C27 1.302(9), Y1−O1−C1 99.6(4), O1−C1−N1 115.0(6), C1−N1−Y1 90.3(4), N1−Y1−O1 54.99(17), Y1−O2−C14 99.8(4), O2−C14−N2 116.3(6), C14−N2−Y1 88.9(4), N2−Y1−O2 54.90(18), Y1−O3−C27 97.2(4), O3−C27−N3 114.8(6), C27−N3−Y1 93.4(4), N3−Y1−O3 54.08(16).

Figure 2 shows the solid-state molecular structure of **7**, which is a centrosymmetric dimer, with each yttrium atom having three amidate ligands. One amidate ligand is bridging to another yttrium atom through the amidate oxygen. Side-on bonding of the amidate ligand, resulting in a η^3 hapticity, has been suggested for complexes resulting from isocyanate insertions into Ln−C bonds.[52] In this case, the amidate scaffold is coplanar with the yttrium atom and ligand denticity is best described as κ^2.

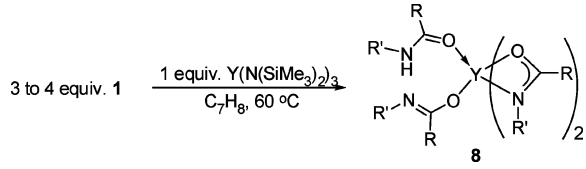
In an attempt to prepare a 6-coordinate, monomeric, tris(amidate) complex, 3 equiv of proligand **1** were reacted with $Y(N(SiMe_3)_2)_3$ in a non-coordinating solvent at 60 °C. The resultant air and moisture sensitive microcrystalline product (**8**) was isolated from warm toluene in poor yield (12%). The residual material from the reaction was insoluble in common organic solvents, consistent with the formation of aggregate species. Complex **8** could not be fully characterized, although the data from the X-ray crystallographic studies of a low quality crystal were satisfactory for establishing connectivity (Scheme 2, Supporting Information, Table S1). Two of the ligands are bound as bidentate amidates, as seen previously, while one monodentate amidate ligand, bound through the oxygen only, displays the hemilabile coordination mode that can be adopted by this ligand framework. Finally, the fourth ligand is a neutral amide, also bound through the oxygen. It is evident by ^1H NMR spectroscopy that one neutral amide is incorporated as a donor ligand, as the amide N−H signal can be seen as a

(64) Mao, L.; Shen, Q.; Xue, M. *Organometallics* **1997**, *16*, 3711.

(65) Data was processed using the SQUEEZE function of the PLATON software to remove disordered THF. Speck, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

(66) Data was processed using the SQUEEZE function of the PLATON software to remove disordered hexanes. Speck, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

Scheme 2. Formation of Complex **8**

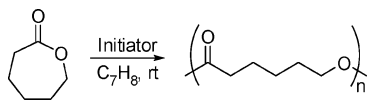


highly deshielded broad singlet at approximately δ 11. Also in the ^{1}H NMR spectrum, the methyl groups and the methine protons for all diisopropylphenyl substituents are seen as broad singlets or multiplets, respectively, indicating the rapid exchange of proton and coordination modes between the ligands on the NMR time scale.

In non-coordinating solvent, even strict control of the reaction stoichiometry (3 proligands to 1 Y) consistently gave evidence (signal at δ 11 in the ^{1}H NMR spectrum) for formation of product **8** in poor yield. Interestingly, product **8** can also be prepared in situ on NMR tube scale by addition of 1 equiv further of proligand **1** to complex **4**, via THF displacement by the neutral amide group. Furthermore, pyridine has also been shown to add to complex **4**, also resulting in displacement of coordinated THF.

As demonstrated by NMR spectroscopic investigations, the ancillary amidate ligands in complex **4** are highly fluxional and additional donors can be easily introduced to the metal center. Thus, when complex **4** was reacted with complex **5**, a scrambling of the ligands occurred, as seen by ^{1}H NMR spectroscopy. The signals for the methylene protons of the THF molecules shifted from δ 4.25 ppm to δ 3.84 ppm, indicating loss of bound THF, and multiple signals were observed for the diisopropyl substituents, as well as naphthyl aryl signals. This reaction occurred immediately at room temperature, and no further change in the ^{1}H NMR spectrum was seen when the solution was heated to 110 °C. Attempts to isolate a mixed amidate yttrium complex have been unsuccessful. In solution phase, it is apparent that the amidate ligands are rapidly exchanging and are thought to exchange through a mechanism that takes advantage of the potential bridging mode of the ligand as seen in complex **7** and ligand hemilability as observed in complex **8**.

The hemilability of the amidate scaffold, and the ease with which the donor ligand can be displaced led us to consider yttrium complexes **4**, **5**, and **6** as being sterically accessible Lewis acids for a range of potential Lewis basic donors. Consequently, investigations using complexes **4**, **5**, and **6** as initiators in ε-caprolactone ring-opening polymerization have been performed and compared with other known yttrium ε-caprolactone polymerization initiators. These preliminary results show that these new homoleptic amidate complexes are very effective initiators for the preparation of high-molecular weight polycaprolactone, a biodegradable polyester.



The commercial synthesis of biodegradable polymers by ring-opening polymerization of lactones with metal-alkoxides, including lanthanide and group 3 complexes, results in the efficient preparation of these desirable polymeric materials.[68−72] Here, complexes **4**, **5**, and **6** can be used as initiators for this process (Table 3, Entries 1−6).[73] ε-Caprolactone is added directly to a stirring solution of a 1.2 mM (for [M]/[I] = 225) toluene solution of initiator. The reactions are stirred vigorously for 15 min under inert atmosphere, exposed to air, and then quenched with 1 M HCl. The polymer can be isolated by precipitation from cold petroleum ether. The molecular weights obtained in entries 1−4, are among the highest molecular weights observed for rare-earth metal initiated ε-caprolactone polymerization.[5,7,8,29,74] However, when comparing entries 1−4, the yield of the polymer is decreased as the monomer to initiator ratio ([M]/[I]) is increased. This may be due to bulk transfer properties, resulting in an increase in chain termination mechanisms as the concentration of monomer is increased.[75,76] From these results the [M]/[I] ratio of 225 was regarded as the optimized ratio (as shown in entry 3 where polymer yield and molecular weight were maximized for compound **4**) and was used for studies with complexes **5** and **6** as initiators (Table 3, entries 5−6). The theoretical M_w value for a [M]/[I] of 225:1 is calculated to be 2.57×10^4 g mol^{-1}. The M_w obtained by complexes **4**, **5**, and **6** are much larger than calculated, suggesting slow initiation followed by rapid polymerization

Table 3. Summary of Ring-Opening Polymerization of ε-Caprolactone

entry	I	[M]/[I]	yield (%)[c]	M_w[d] ($\times 10^4$) g mol^{-1}	PDI[d]	M_w[e] ($\times 10^4$) g mol^{-1}	PDI[e]
1	**4**[a]	50	95	24.7	2.56	11.8	1.62
2	**4**[a]	100	96	27.8	2.40	10.2	1.38
3	**4**[a]	225	91	32.5	2.12	10.7	1.28
4	**4**[a]	500	63	31.7	2.20	10.7	1.28
5	**5**[a]	225	80	41.7	2.29	15.8	1.43
6	**6**[a]	225	56	17.8	2.47	5.57	1.41
7[45]	**9**[a]	500	100	7.98	1.81		
8[67]	**10**[b]	224	65	151	2.90		

[a] General polymerization conditions: in toluene, 15 min of stirring, 25 °C. [b] Toluene, 1.5 h, 25 °C. [c] Yield = weight of polymer obtained/weight of monomer used. [d] Measured by GPC calibrated with standard polystyrene samples. [e] Measured by GPC (triple detection) equipped with differential refractometer (Waters), viscometer, and laser-light scattering detectors (Wyatt).

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(72) Sheng, H.; Xu, F.; Yao, Y.; Zhang, Y.; Shen, Q. *Inorg. Chem.* **2007**, *46*, 7722.
(73) It should be noted that each entry has been completed in triplicate to ensure validity of values for yield, molecular weight, and PDI. Two different methods of GPC results are reported for comparative reasons. These different conditions are known to give variable results for this class of polymers. Refer to (a) Huang, Y. *Int. J. Polym. Anal. Charact.* **2003**, *8*, 383.
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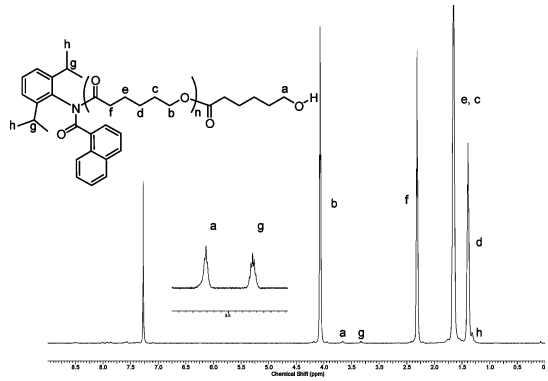

Figure 3. ^{1}H NMR (600 MHz) spectrum (in $CDCl_3$) of poly(ε-caprolactone) using initiator **4**.

by small quantities of catalytically active species. The polymer produced using initator **4** and a 10:1 monomer to initiator ratio was evaluated using end group analysis by ^{1}H NMR spectroscopy, as shown in Figure 3. The incorporation of one ligand in the polymer chain is observed, as evidenced by the signal at δ 3.66, (for the OH terminus of the polymer) that integrates for 2 protons, as does the multiplet at δ 3.33 for the methine protons of the ligand isopropyl substituents (also 2 protons). This is consistent with the mechanism of polymerization proceeding through ligand promoted initiation to produce a polymer with amide **1** as the terminus. The efficiency of this step continues to be an area of investigation within the group and is a current focus in the development of new initiators with improved reactivity patterns.

The PDI values are typical for rare-earth initiated ring-opening polymerization of ε-caprolactone. The more sterically accessible complex **5** gave a reduced yield in comparison to **4**, but also a higher molecular weight and slightly broader PDI. The impact of the efficiency of polymerization initiation is also apparent in the changes in PDI between complexes **4**, **5**, and **6**. By placing the electron-withdrawing group CF_3 in the amidate scaffold, as in complex **6**, the efficiency of initiating the ring-opening polymerization diminished (as detected by the lower polymer yield, lower molecular weight polymer, and higher PDI). These data indicate that complexes **4**, **5**, and **6** are already good initiators of ring-opening ε-caprolactone and that the amidate scaffold provides an easily varied ligand set that can be exploited for enhancing reactivity.

Similar rare-earth complexes to that of the amidates, such as the amidinates, have been found to be active for the initiation of the ring-opening polymerization of ε-caprolactone. For example, the homoleptic neodymium amidinate complex, $[CyNC(Me)NCy]_3Nd$ (**9**) (Table 3, Entry 7), forms polymer of a moderate molecular weight (7.98×10^4 g mol^{-1}) with a slightly narrower PDI value of 1.81. Although the analogous yttrium amidinate complex was prepared, no polymerization results were reported.[45] Polymerization reactivity of some rare-earth complexes has been found to increase with increasing radii, since a less crowded coordination environment (resulting from a larger metal radius) facilitates monomer coordination and subsequent insertion.[1,77] This suggests that neodymium compounds should be more reactive than yttrium (since Nd is larger than Y). The tris(amidate) complex **4** compares favorably to the neodymium complex, indicating the amidate scaffold may enhance reactivity over the amidinate ligand set. Interestingly, in slightly different conditions (1.5 h instead of 15 min.) the starting material to form **4**, **5**, and **6**, $Y(N(SiMe_3)_2)_3$ (**10**) (Table 3, Entry 8) can form very large molecular weight polymers, with a broad PDI.[67] This shows that the amidate complexes can yield polymers of higher molecular weights than similar amidinate complexes, as well as improved PDI values over $Y(N(SiMe_3)_2)_3$, and suggests that this easily accessed and tunable family of initiators should be investigated further for optimized reactivity in the ring-opening polymerization of lactones.

Summary and Conclusions

In summary, a reliable synthetic route has been developed for the first, fully characterized examples of monomeric tris(amidate) complexes of yttrium. The characterized homoleptic tris(amidate) complexes of yttrium (**4**, **5**, and **6**) were synthesized directly from sterically bulky amide proligands and $Y(N(SiMe_3)_2)_3$ in high yields. Spectroscopic studies of these 7-coordinate compounds indicate that the amidate ligands are very fluxional, and neutral donor ligands are readily exchanged, making them interesting initiators for the ring-opening polymerization of lactones. These complexes have high activity as ε-caprolactone polymerization initiators, producing large molecular weight biodegradable polymers, and the modest variations in ligand structure included here have resulted in notable changes in polymerization initiation activity. On-going research will take advantage of the tunable amidate ligand set to generate new rare-earth amidate complexes as optimized initiators for the ring-opening polymerization of a variety of cyclic lactones including ε-caprolactone and lactide.

Acknowledgment. The authors thank UBC, CFI, BCKDF, and DuPont for financial support of this work. L.J.E.S. thanks UBC and MEC for scholarships, as well as the Gates group at the University of British Columbia, and Alissa Han of the Holdcroft group at Simon Fraser University for technical assistance with GPC measurements.

Supporting Information Available: Crystallographic information files (CIF) of complexes **4**, and **7**, as well as solid-state molecular structure data for complex **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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