Synthesis and Characterization of Heterobimetallic Oxo-Bridged Aluminum–Rare Earth Metal Complexes

Jingjun Hao,[†] Jianfeng Li,[†] Chunming Cui,^{*,†} and Herbert W. Roesky[‡][†]State Key Laboratory and Institute of Element-Organic Chemistry, Nankai University, Tianjin 300071[‡]People's Republic of China; Institute of Inorganic Chemistry, University of Goettingen, 37077 Goettingen, Germany

S Supporting Information

ABSTRACT: Reaction of the aluminum hydroxide $\text{LAl}(\text{OH})[\text{C}(\text{Ph})\text{CH}(\text{Ph})]$ (**1**, $\text{L} = \text{HC}[(\text{CMe})(\text{NAr})]_2$, $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) with $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ yielded the oxo-bridged heterobimetallic yttrium dialkyl complex $\text{LAl}[\text{C}(\text{Ph})\text{CH}(\text{Ph})](\mu\text{-O})\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ (**2**). Alkane elimination reaction of **2** with 2-(imino)pyrrole $[\text{NN}]\text{H}$ ($[\text{NN}]\text{H} = 2\text{-(ArN=CH)-5-}t\text{BuC}_4\text{H}_2\text{NH}$) afforded the yttrium monoalkyl complex $\text{LAl}[\text{C}(\text{Ph})\text{CH}(\text{Ph})](\mu\text{-O})\text{Y}(\text{CH}_2\text{SiMe}_3)[\text{NN}](\text{THF})_2$ (**5**). Alternatively, **5** can be prepared in high yield by reaction of **1** with $[\text{NN}]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ (**3**). The analogous samarium alkyl complex $\text{LAl}[\text{C}(\text{Ph})\text{CH}(\text{Ph})](\mu\text{-O})\text{Sm}(\text{CH}_2\text{SiMe}_3)[\text{NN}](\text{THF})_2$ (**6**) was prepared similarly. Reactions of **5** and **6** with 1 equiv of $i\text{PrOH}$ yielded the corresponding alkoxy complexes **7** and **8**, respectively. The molecular structures of **3**, **6**, and **8** have been determined by X-ray single-crystal analysis. Complexes **2**, **3**, **5**, **7**, and **8** have been investigated as lactide polymerization initiators. The heterobimetallic alkoxy **8** is highly active to yield high molecular weight ($M_n = 6.91 \times 10^4$) polylactides with over 91% conversion at the lactide-to-initiator molar ratio of 2000.

INTRODUCTION

Rare earth metal complexes incorporating non-Cp type of ligands have attracted much attention since their interesting structural features and applications in molecular catalysis such as alkene and lactide polymerization reactions and intramolecular hydroamination of alkenes.¹ A number of bulky organic ligands have been employed for the stabilization of well-defined rare earth metal alkyls, amides, and alkoxydes. In polymerization reactions, aluminum alkyls and aluminoxanes are frequently used as cocatalysts.² Consequently, the studies on the reactions of rare earth metal complexes with aluminum complexes have been extensively performed for the understanding polymerization mechanism.³ An alternative approach for the investigation of oxo-bridged aluminum–group 4 metal complexes indicated that these compounds are not only excellent for the polymerization reactions with low Al/Zr ratios but also display interesting structural features as indicated by the large Al–O–M angles and short M–O bond lengths.⁴ Inspired by these successful results, we are interested in the synthesis, characterization, and lactide polymerization behaviors of oxo-bridged aluminum–rare earth metal (Al–O–Ln) complexes. The known oxo-bridged Al–O–Ln complexes are very limited and only confined to those containing Cp_2Ln and β -diketiminato–Ln fragments.⁵ Bimetallic Al–O–Ln complexes possessing a reactive Ln–E σ -bond (E = CR_3 , NR_2 , OR), to the best of our knowledge, have not been reported so far.

Ring-opening polymerization (ROP) of lactide with well-defined metal complexes has been one of the recent focuses for the preparation of biodegradable polylactides.⁶ Both rare-earth metal and aluminum complexes have been investigated as catalysts for the ROP. By incorporating suitable ancillary ligands, aluminum alkoxydes exhibit relatively low rate but well-controlled stereochemistry over the polymerization reactions.⁷ In contrast,

rare-earth metal complexes generally display remarkable high activity.⁸ It has been recently shown that several lanthanide complexes initiate the polymerization of *rac*-lactide in stereospecific manners.⁹ However, oxo-bridged Al–Ln complexes have not been explored as ROP catalysts. Recent studies have revealed that aluminum hydroxides can function as building blocks for the synthesis of oxo-bridged heterometallic complexes.^{4,5,10} We and others have previously reported several routes to prepare organoaluminum hydroxides that are stabilized by the bulky β -diketiminato ligand L ($\text{HC}[(\text{CMe})(\text{NAr})]_2$, $\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$).^{4a,11} Herein, we report on the synthesis and characterization of novel heterobimetallic Al–O–Ln alkyls and alkoxydes, prepared by alkane elimination reactions of $\text{LAl}(\text{OH})(\text{CPhCHPh})$ (**1**) with Ln (Ln = Y, Sm) alkyls. In addition, lactide polymerization reactions with these complexes have also been investigated.

EXPERIMENTAL SECTION

All operations were carried out under an atmosphere of dry argon or nitrogen using modified Schlenk line and glovebox techniques. All solvents were freshly distilled from sodium and degassed immediately prior to use. Elemental analyses were carried out on an Elemental Vario EL analyzer. The ^1H and ^{13}C NMR spectroscopic data were recorded on a Varian Mercury Plus 400 and Bruker AV400 spectrometers. Infrared spectra were recorded on a Bio-Rad FTS 6000 spectrometer. The molecular weight and the dispersity of the polymers were measured by GPC analysis. $\text{LAl}(\eta^2\text{-C}_2\text{Ph}_2)$,¹² aryliminopyrrole $[\text{NN}]\text{H}$,¹³ $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ ¹⁴ were synthesized according to published procedures, and $\text{Sm}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_3$ was prepared similarly.

Received: January 25, 2011

Published: July 15, 2011

Synthesis of $\text{LaI}(\text{OH})[\text{C}(\text{Ph})\text{CH}(\text{Ph})]$ (1). To a solution of $\text{LaI}(\eta^2\text{-C}_2\text{Ph}_2)$ (3.1 g, 5.0 mmol) in diethyl ether (100 mL) at -78°C was added a solution of water (0.09 mL, 5.0 mmol) in diethyl ether (50 mL). The orange solution immediately turned to pale yellow. The mixture was warmed to room temperature and stirred for additional 4 h. The volatiles were removed under vacuum, and the remaining solid was extracted with *n*-hexane (50 mL). It was filtered, the filtrate was concentrated and stored in a freezer at -40°C overnight to give white crystals of **1** (2.63 g, 82%). Mp: $166\text{--}168^\circ\text{C}$. ^1H NMR (C_6D_6 , 400 MHz): δ 0.65 (s, 1H, OH), 1.08 (t, $J = 6.4$ Hz, 12H, CHMe_2), 1.16 (d, $J = 6.8$ Hz, 6H, CHMe_2), 1.32 (d, $J = 6.8$ Hz, 6H, CHMe_2), 1.59 (s, 6H, $\beta\text{-CMe}$), 3.39 (sept, 2H, $J = 6.80$ Hz, CHMe_2), 3.75 (sept, 2H, $J = 6.80$ Hz, CHMe_2), 5.00 (s, 1H, $\gamma\text{-CH}$), 6.31 (d, 2H, $J = 7.6$ Hz, Ar-H), 6.36 (s, 1H, $\text{C}=\text{CHPh}$), 6.74–6.97 (m, 10H, Ar-H), 7.17–7.27 (m, 6H, Ar-H). ^{13}C NMR (C_6D_6 , 100 MHz): δ 23.40 ($\beta\text{-Me}$), 24.36, 24.59, 24.93, 25.29 (CHMe_2), 27.85, 29.19 (CHMe_2), 98.62 ($\gamma\text{-C}$), 123.98, 124.32 (Ar), 125.26 ($\text{C}=\text{CHPh}$), 126.26, 126.67, 127.42, 127.92, 128.49, 129.63, 139.23, 140.62, 141.48, 143.57 (Ar), 147.95 (Al-C), 170.27 (NC). IR (KBr, cm^{-1}): 3482 (m, OH). Anal. Calcd for $\text{C}_{43}\text{H}_{53}\text{AlN}_2\text{O}$ (640.39): C, 80.59; H, 8.34; N, 4.37. Found: C, 80.53; H, 8.30; N, 4.48.

Synthesis of $\text{LaI}[\text{C}(\text{Ph})\text{CH}(\text{Ph})](\mu\text{-O})\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ (2). To a *n*-hexane solution (60 mL) of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (0.98 g, 2.0 mmol) was added a solution of **1** (1.28 g, 2.0 mmol) in *n*-hexane (60 mL) at -78°C . The mixture was warmed to 0°C and stirred for additional 4 h. The solution was concentrated (ca. 20 mL) and stored in a freezer at -40°C overnight to give $2 \cdot 0.5\text{C}_6\text{H}_{14}$ as colorless crystals (1.60 g, 76%). Mp: 125°C (dec.). ^1H NMR (C_6D_6 , 400 MHz): δ -0.90 (s, 4H, CH_2SiMe_3), 0.33 (s, 18H, CH_2SiMe_3), 1.06 (d, $J = 4.2$ Hz, 12H, CHMe_2), 1.17 (d, $J = 6.4$ Hz, 6H, CHMe_2), (s, 8H, THF), 1.29 (br, 14H, THF and $\beta\text{-Me}$), 1.41 (d, $J = 6.4$ Hz, 6H, CHMe_2), 3.49 (br, 12H, THF and CHMe_2), 4.88 (s, 1H, $\gamma\text{-CH}$), 6.88–7.59 (m, 16H, Ar-H). ^{13}C NMR (C_6D_6 , 100 MHz): δ 5.10 (s, SiMe_3), 24.11 (CHMe_2), 24.56 (d, $J = 6.0$ Hz, CH_2SiMe_3), 25.48 (THF), 26.14, 26.31 ($\beta\text{-Me}$), 27.77, 28.66 (CHMe_2), 69.84 (THF), 100.70 ($\gamma\text{-C}$), 124.29, 124.69 (Ar), 126.10 ($\text{C}=\text{CHPh}$), 126.81, 127.40, 127.81, 130.24, 130.77, 140.47, 140.80, 142.98, 144.90, 145.63 (Ar), 147.70 (Al-C), 170.81 (NC). Anal. Calcd for $\text{C}_{59}\text{H}_{90}\text{AlN}_2\text{O}_3\text{Si}_2\text{Y} \cdot 0.5\text{C}_6\text{H}_{14}$ (1090.50): C, 68.29; H, 8.97; N, 2.57. Found: C, 67.64; H, 8.85; N, 2.38.

Synthesis of $[\text{NN}]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ (3). To a solution (60 mL) of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (0.98 g, 2.0 mmol) in *n*-hexane was added a solution of $[\text{NN}]\text{H}$ (0.62 g, 2.0 mmol) in 20 mL of *n*-hexane at -78°C . The mixture was allowed to warm to room temperature and stirred overnight. It was concentrated to ca. 5 mL, and then THF (3 mL) were added. The solution was stored at -40°C overnight to give colorless crystals of **3** (1.1 g, 75%). Mp: $101\text{--}103^\circ\text{C}$. ^1H NMR (C_6D_6 , 400 MHz): δ -0.19 (s, 4H, CH_2SiMe_3), 0.27 (s, 18H, CH_2SiMe_3), 0.96 (d, $J = 6.6$ Hz, 6H, CHMe_2), 1.14 (d, $J = 6.8$ Hz, 6H, CHMe_2), 1.26 (br, 8H, THF), 1.69 (s, 9H, CMe_3), 3.11 (m, 2H, CHMe_2), 3.58 (br, s, 8H, THF), 6.40 (d, $J = 3.6$ Hz, 1H, pyr-H), 6.81 (d, $J = 3.6$ Hz, 1H, pyr-H), 6.95–7.02 (m, 3H, Ar-H), 7.51 (s, 1H, $\text{N}=\text{CH}$). ^{13}C NMR (C_6D_6 , 100 MHz): δ 4.46 (SiMe_3), 22.65 (CHMe_2), 25.42 (THF), 25.97, 28.71 (CHMe_2), 32.29 (CMe_3), 34.51 (CMe_3), 37.47 (d, $J_{\text{YC}} = 52.3$ Hz, $\text{Y}-\text{CH}_2$), 69.11 (THF), 110.88 (pyr), 123.72 (pyr), 126.01, 126.37 (Ar), 134.27 (5-pyr), 141.91, 148.38 (Ar), 161.94 (2-pyr), 166.14 (NC). Anal. Calcd for $\text{C}_{37}\text{H}_{67}\text{N}_2\text{O}_2\text{Si}_2\text{Y}$ (717.02): C, 61.98; H, 9.42; N, 3.91. Found: C, 61.51; H, 9.51; N, 3.62.

Synthesis of $[\text{NN}]\text{Sm}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_2$ (4). **4** was prepared similarly as described for **3** and obtained as orange crystals (0.84 g, 54%). Mp: $84\text{--}86^\circ\text{C}$. ^1H NMR (C_6D_6 , 400 MHz): δ -4.43 (s, 9H, CMe_3), 0.31 (s, 6H, CHMe_2), 0.70 (br, 8H, THF), 1.00 (s, 18H, CH_2SiMe_3), 1.26 (s, 6H, CHMe_2), 1.66 (m, 2H, CHMe_3), 2.53 (br, 8H, THF), 5.50 (m, 2H, Ar-H), 5.82 (m, 1H, Ar-H), 6.61 (m, 1H, pyr-H), 8.74 (m, 1H, pyr-H), 9.02 (br, s, 4H, CH_2SiMe_3). ^{13}C NMR (C_6D_6 , 100 MHz): δ 3.13 (SiMe_3), 21.56 (CHMe_2), 24.30, 25.64 (CHMe_2), 26.49 (THF), 27.37 (CMe_3), 30.18 (CMe_3), 67.95 (THF), 109.02 (pyr), 121.63 (pyr),

123.43, 127.53 (Ar), 137.12 (5-pyr), 142.07, 149.09 (Ar), 165.12 (2-pyr), 171.60 (NC); the $\text{Sm}-\text{CH}_2$ ^{13}C NMR signal could not be located. Anal. Calcd for $\text{C}_{37}\text{H}_{67}\text{N}_2\text{O}_2\text{Si}_2\text{Sm}$ (778.47): C, 57.09; H, 8.67; N, 3.60. Found: C, 56.54; H, 8.70; N, 3.28.

Synthesis of $\text{LaI}[\text{C}(\text{Ph})\text{CH}(\text{Ph})](\mu\text{-O})\text{Y}(\text{CH}_2\text{SiMe}_3)[\text{NN}](\text{THF})_2$ (5). To solution (20 mL) of **3** (0.72 g, 1.00 mmol) in toluene was added a solution of **1** (0.64 g, 1.00 mmol) in toluene (20 mL) at room temperature. After it was stirred for 4 h, volatiles were removed under vacuum. The remaining solid was dissolved in THF/*n*-hexane (1:1) and stored at -40°C overnight to give **5** as colorless crystals (1.12 g, 86%). Mp: $138\text{--}141^\circ\text{C}$. ^1H NMR (C_6D_6 , 400 MHz): δ -0.92 , -0.88 (dd, $^2J_{\text{HH}} = 11.2$ Hz, $^2J_{\text{YH}} = 3.2$ Hz, 1H, CH_2SiMe_3), 0.04, 0.08 (dd, $^2J_{\text{HH}} = 11.2$ Hz, $^2J_{\text{YH}} = 4.0$ Hz, 1H, CH_2SiMe_3), 0.30 (s, 9H, CH_2SiMe_3), 0.81 (d, $J = 6.4$ Hz, 3H, CHMe_2), 0.95 (d, $J = 6.4$ Hz, 3H, CHMe_2), 1.01 (d, $J = 7.2$ Hz, 3H, CHMe_2), 1.04 (d, $J = 6.4$ Hz, 6H, CHMe_2), 1.10 (d, $J = 6.4$ Hz, 6H, CHMe_2), 1.14 (d, $J = 6.4$ Hz, CHMe_2), 1.37 (d, $J = 6.8$ Hz, 3H, CHMe_2), 1.39 (br, 8H, THF), 1.46 (d, $J = 6.4$ Hz, 3H, CHMe_2), 1.55 (d, $J = 6.8$ Hz, 3H, CHMe_2), 1.63 (s, 3H, $\beta\text{-Me}$), 1.64 (d, $J = 6.8$ Hz, 3H, CHMe_2), 1.73 (s, 3H, $\beta\text{-Me}$), 1.85 (s, 9H, CMe_3), 2.96 (m, 1H, CHMe_2), 3.07–3.22 (m, 2H, CHMe_2), 3.50 (m, 2H, CHMe_2), 3.57 (br, 8H, THF), 4.44 (m, 1H, CHMe_2), 5.21 (s, 1H, $\gamma\text{-CH}$), 6.28 (s, 1H, $\text{C}=\text{CH}$), 6.42–6.44 (d, 4H, Ar-H), 6.46 (d, $J = 3.6$ Hz, 2H, pyr-H), 6.62–6.70 (m, 3H, Ar-H), 6.75–6.78 (t, 1H, Ar-H), 6.84–6.89 (m, 3H, Ar-H), 6.91 (d, $J = 3.6$ Hz, 2H, pyr-H), 6.95–7.03 (m, 3H, Ar-H), 7.07–7.09 (m, 1H, Ar-H), 7.17–7.22 (m, 2H, Ar-H), 7.27–7.35 (m, 2H, Ar-H), 7.65 (s, 1H, $\text{CH}=\text{N}$). ^{13}C NMR (C_6D_6 , 100 MHz): δ 4.49 (SiMe_3), 21.94, 22.97 (CHMe_2), 23.97, 24.40, 24.57, 24.64 (CHMe_2), 24.77, 25.13, 25.24 (CHMe_2), 25.70 (THF), 25.82 (CHMe_2), 26.76, 26.95 ($\beta\text{-Me}$), 27.76, 28.02, 28.33, 28.43, 28.47, 28.59, 29.38, 30.82 (CHMe_2), 31.43 ($\text{Y}-\text{CH}_2\text{SiMe}_3$), 32.38 (CMe_3), 34.66 (CMe_3), 67.85 (THF), 101.55 ($\gamma\text{-C}$), 110.51 (pyr), 123.29 (pyr), 123.87, 124.03, 124.27, 124.60, 124.86, 125.69, 125.75 (Ar), 126.16 ($\text{C}=\text{CHPh}$), 127.06, 127.27, 128.56, 129.76, 133.80 (Ar), 139.60 (5-pyr), 141.52, 141.69, 142.80, 142.96, 143.14, 144.37, 144.67, 144.86, 145.44, 146.10 (Ar), 149.39 (Al-C), 162.42 (2-pyr), 165.76 ($\text{CH}=\text{N}$), 169.62, 169.99 (NC). Anal. Calcd for $\text{C}_{76}\text{H}_{108}\text{AlN}_4\text{O}_3\text{Si}_4\text{Y} \cdot 0.5\text{C}_6\text{H}_{14}$ (1312.76): C, 72.28; H, 8.83; N, 4.27. Found: C, 71.83; H, 8.75; N, 4.18.

Synthesis of $\text{LaI}[\text{C}(\text{Ph})\text{CH}(\text{Ph})](\mu\text{-O})\text{Sm}(\text{CH}_2\text{SiMe}_3)[\text{NN}](\text{THF})_2$ (6). **6** was prepared similarly as described for **5** and obtained as pale-yellow crystals (1.1 g, 85%). Mp: 172°C (dec.). ^1H NMR (C_6D_6 , 400 MHz): δ -5.52 (br, m, 1H, CHMe_2), -3.33 (br, s, 9H, CMe_3), -2.88 (br, m, 1H, CHMe_2), -1.33 (s, 3H, $\beta\text{-Me}$), -0.45 (s, 3H, CHMe_2), 0.27 (s, 3H, CHMe_2), 0.67 (br, s, 9H, CH_2SiMe_3), 0.81 (br, s, 3H, CHMe_2), 0.95 (br, 4H, THF), 1.10 (t, 1H, Ar-H), 1.32 (d, $J = 6.4$ Hz, 3H, CHMe_2), 1.45 (t, $J = 5.2$ Hz, 6H, CHMe_2), 1.64 (d, $J = 6.4$ Hz, 3H, CHMe_2), 1.70 (d, $J = 6.0$ Hz, 3H, CHMe_2), 1.92 (s, 3H, $\beta\text{-Me}$), 2.62 (br, 3H, CHMe_2), 2.88 (br, s, 3H, CHMe_2), 3.04 (d, $J = 4.0$ Hz, 3H, CHMe_2), 3.35 (br, m, 4H, THF), 4.02 (m, 1H, pyr-H), 4.50 (m, 2H, Ar-H), 4.61 (br, m, 1H, Ar-H), 5.14 (d, $J = 6.4$ Hz, 1H, $\gamma\text{-CH}$), 6.14 (t, 1H, Ar-H), 6.55 (m, 1H, pyr-H), 6.69 (br, s, 3H, CHMe_2), 6.79 (s, 2H, CHMe_2), 6.91 (t, 1H, Ar-H), 7.05–7.12 (m, 5H, Ar-H), 7.45–7.61 (m, 7H, Ar-H), 7.70 (s, 2H, CHMe_2), 7.81 (m, 1H, Ar-H), 8.28 (s, 1H, $\text{C}=\text{CHPh}$), 8.39 (s, 1H, $\text{CH}=\text{N}$), 9.45 (br, s, 1H, CH_2SiMe_3), 10.60 (br, s, 1H, CH_2SiMe_3). ^{13}C NMR (C_6D_6 , 100 MHz): δ 2.82 (SiMe_3), 19.61 (CHMe_2), 23.78, 24.27, 24.44, 24.62, 24.68 (CHMe_2), 24.80, 25.22 ($\beta\text{-Me}$), 25.41 (THF), 27.40, 28.21, 29.00, 29.19, 29.26 (CHMe_2), 30.34 (CMe_3), 31.17 (CHMe_2), 31.55 (CMe_3), 68.52 (THF), 101.37 ($\gamma\text{-C}$), 108.66 (pyr), 121.19 (pyr), 122.98, 123.70, 124.12, 125.05, 125.28, 125.39, 125.97, 126.39 (Ar), 127.39 ($\text{C}=\text{CHPh}$), 129.66, 130.46 (Ar), 135.95 (5-pyr), 140.36, 141.00, 143.94, 144.19, 144.52, 144.64, 145.17, 145.25, 146.19, 146.25 (Ar), 148.51 (Al-C), 164.69 (2-pyr), 168.45 ($\text{CH}=\text{N}$), 170.23, 170.73 (NC); the $\text{Sm}-\text{CH}_2$ ^{13}C NMR signal could not be located. Anal. Calcd for $\text{C}_{72}\text{H}_{100}\text{AlN}_4\text{O}_2\text{Si}_4\text{Sm} \cdot 0.5\text{C}_6\text{H}_{14}$ (1302.10): C, 69.18; H, 8.28; N, 4.30. Found: C, 68.72; H, 8.35; N, 4.06.

Synthesis of $\text{LAl}[\text{C}(\text{Ph})\text{CH}(\text{Ph})](\mu-\text{O})\text{Y}(\text{O}i\text{Pr})[\text{NN}](\text{THF})_2$ (7).

To a toluene solution (20 mL) of **5** (1.32 g, 1.00 mmol) was added a solution of *i*PrOH (0.066 g, 1.10 mmol) in 5 mL of toluene at room temperature. After it was stirred for 10 h, volatile materials were removed under vacuum. The remaining solid was dissolved in *n*-hexane. The solution was stored at -40°C for 24 h to give **7** as colorless crystals (0.70 g, 58%). Mp: $131-133^\circ\text{C}$. ^1H NMR (C_6D_6 , 400 MHz): δ 0.86–0.90 (t, 6H, $J = 6.8$ Hz, CHMe_2), 0.95 (d, 3H, $J = 6.8$ Hz, CHMe_2), 1.04 (d, 3H, $J = 6.8$ Hz, CHMe_2), 1.10 (t, $J = 5.6$ Hz, 12H, CHMe_2), 1.14 (d, 3H, $J = 7.6$ Hz, CHMe_2), 1.18 (d, 3H, $J = 6.8$ Hz, CHMe_2), 1.22 (br, 4H, THF), 1.31 (d, 3H, $J = 6.4$ Hz, CHMe_2), 1.34 (d, 3H, $J = 7.6$ Hz, CHMe_2), 1.57 (d, 3H, $J = 6.8$ Hz, OCHMe_2), 1.61 (s, 3H, $\beta\text{-CMe}$), 1.69 (s, 3H, $\beta\text{-CMe}$), 1.74 (d, 3H, $J = 6.4$ Hz, OCHMe_2), 1.82 (s, 9H, CMe_3), 3.13 (m, 2H, CHMe_2), 3.42 (m, 1H, CHMe_2), 3.57 (br, 4H, THF), 3.73 (m, 2H, CHMe_2), 4.37 (m, 1H, CHMe_2), 4.61 (sept, 1H, OCHMe_2), 5.15 (s, 1H, $\gamma\text{-CH}$), 6.12 (s, 1H, $\text{C}=\text{CH}$), 6.46–6.48 (d, 2H, Ar-H), 6.52 (br, s, 1H, pyr-H), 6.68 (s, 4H, Ar-H), 6.70 (br, s, 1H, pyr-H), 6.74–7.06 (m, 9H, Ar-H), 7.21–7.37 (m, 4H, Ar-H), 7.66 (s, 1H, $\text{N}=\text{CH}$). ^{13}C NMR (C_6D_6 , 100 MHz): δ 21.89 (CHMe_2), 23.76, 24.22, 24.54, 25.21 (CHMe_2), 25.66 (THF), 26.38, 27.03 ($\beta\text{-Me}$), 27.69, 27.90, 27.97, 28.21, 28.45, 28.50, 28.65, 29.17, 29.43 (CHMe_2 and OCHMe_2), 31.76 (CMe_3), 34.66 (CMe_3), 67.99 (THF), 71.05 (OCHMe_2), 100.14 ($\gamma\text{-C}$), 110.19 (pyr), 123.26 (pyr), 123.53, 123.82, 124.46, 125.28, 125.51 (Ar), 127.05 ($\text{C}=\text{CHPh}$), 127.49, 127.62, 129.29, 133.85 (Ar), 139.83 (5-pyr), 140.41, 141.70, 142.62, 142.68, 144.11, 144.22, 145.00, 145.57, 146.06 (Ar), 149.53 (Al–C), 162.35 (2-pyr), 165.34 ($\text{HC}=\text{N}$), 169.34, 169.49 (NC). Anal. Calcd for $\text{C}_{74}\text{H}_{104}\text{AlN}_4\text{O}_3\text{Y} \cdot 0.5\text{C}_6\text{H}_{14}$ (1256.62): C, 73.60; H, 8.90; N, 4.46. Found: C, 73.18; H, 8.84; N, 4.23.

Synthesis of $\text{LAl}[\text{C}(\text{Ph})\text{CH}(\text{Ph})](\mu-\text{O})\text{Sm}(\text{O}i\text{Pr})[\text{NN}](\text{THF})$ (8).

Similar procedure as described for **7** was employed for the synthesis of **8**. **8** was obtained as pale-yellow crystals (0.66 g 52%). Mp: $137-139^\circ\text{C}$. ^1H NMR (C_6D_6 , 400 MHz): δ –5.23 (br, 1H), –4.77 (br, 1H), –2.88 (s, 9H, CMe_3), –1.05 (s, 3H), –0.95 (d, 3H, $J = 4.8$ Hz, CHMe_2), –0.64 (s, 3H), –0.07 (br, 3H), 0.60 (s, 3H), 1.10 (t, 3H, $J = 7.6$ Hz, CHMe_2), 1.24 (d, 3H, $J = 6.0$ Hz, CHMe_2), 1.50 (br, 4H, THF), 1.63 (d, 3H, $J = 6.0$ Hz, CHMe_2), 1.81 (d, 3H, $J = 6.0$ Hz, CHMe_2), 2.02 (s, 3H), 2.30 (br, 3H), 2.68 (br, 3H), 2.74 (d, 3H, $J = 2.8$ Hz, CHMe_2), 3.07 (d, 3H, $J = 2.8$ Hz, CHMe_2), 3.77 (m, 1H, CHMe_2), 3.99 (m, 1H, CHMe_2), 4.11 (br, 4H, THF), 4.50 (br, 2H, CHMe_2), 5.06 (d, 1H, $J = 7.2$ Hz), 5.83 (br, 1H, CHMe_2), 6.02 (t, 1H, $J = 7.6$ Hz), 6.52 (d, 1H, $J = 7.6$ Hz), 6.58 (s, 1H), 7.06 (t, 4H, $J = 7.2$ Hz), 7.30 (m, 1H, Ar-H), 7.55 (m, 3H, Ar-H), 7.75 (d, 1H, $J = 6.8$ Hz), 8.52 (br, 2H), 8.72 (br, 1H), 10.46 (br, 1H). ^{13}C NMR (C_6D_6 , 100 MHz): δ 19.81, 21.69 (CHMe_2), 23.47, 13.53, 24.46, 24.51, 24.78, 24.83, 25.13, 25.36 (CHMe_2), 25.59 (THF), 26.74, 27.97 ($\beta\text{-Me}$), 28.64, 28.70, 29.25, 30.15, 30.50, 30.62, 30.68 (CHMe_2 and OCHMe_2), 30.89 (CMe_3), 31.70 (CMe_3), 69.65 (br, THF), 70.34 (Sm– OCHMe_2), 99.76 ($\gamma\text{-C}$), 107.84 (pyr), 120.84 (pyr), 122.32, 123.28, 124.43, 124.72, 124.78, 125.45, 125.79 (Ar), 127.13 ($\text{C}=\text{CHPh}$), 129.71, 130.40, 135.37 (Ar), 140.00 (5-pyr), 140.83, 142.60, 143.23, 143.94, 144.35, 144.58, 145.23, 145.39, 146.73 (Ar), 148.70 (Al–C), 163.90 (2-pyr), 164.83 ($\text{CH}=\text{N}$), 169.07, 170.65 (NC). Anal. Calcd for $\text{C}_{74}\text{H}_{104}\text{AlN}_4\text{O}_3\text{Sm} \cdot 0.5\text{C}_6\text{H}_{14}$ (1318.07): C, 70.16; H, 8.49; N, 4.25. Found: C, 69.67; H, 8.23; N, 4.07.

Polymerization of *rac*-Lactide. A typical procedure for polymerization of *rac*-lactide was performed in 100 mL Schlenk flasks. To a mixture an appropriate amount of *rac*-lactide and catalyst (0.02 mmol) was added 15 mL of toluene at room temperature. After polymerization reaction, all volatiles were removed under vacuum and the viscous solid was washed twice with 20 mL of methanol. The remaining solid was dissolved in a small amount of CH_2Cl_2 , and then *n*-hexane was added to incipient precipitation (CH_2Cl_2 /*n*-hexane, 1:4 v/v). The precipitated polymer was collected and dried under vacuum for 24 h. The molecular weight and the dispersities of the resulting polymer were determined by GPC. The ^1H NMR spectra of polylactides samples were recorded in CDCl_3 .

Table 1. Crystallographic Data for **3**, **6**, and **8**

	3	6 · C_7H_8	8 · $0.5\text{C}_6\text{H}_{14}$
formula	$\text{C}_{37}\text{H}_{67}\text{N}_2\text{O}_2\text{-Si}_2\text{Y}$	$\text{C}_{79}\text{H}_{108}\text{AlN}_4\text{O}_2\text{-SiSm}$	$\text{C}_{77}\text{H}_{111}\text{AlN}_4\text{O}_3\text{-Sm}$
fw	717.02	1351.11	1317.02
T (K)	113(2)	113(2)	113(2)
space group	$P12_1/n1$	$Pbca$	$P-1$
a (Å)	10.4948(4)	40.130(8)	10.926(2)
b (Å)	18.2644(8)	18.800(4)	15.241(3)
c (Å)	21.1763(8)	19.107(4)	22.931(5)
α (deg)	90.00	90.00	88.87(3)
β (deg)	94.849(3)	90.00	78.41(3)
γ (deg)	90.00	90.00	70.49(3)
V (Å ³)	4044.6(3)	14415(5)	3521.3(12)
Z	4	8	2
d_{calcd} (g/cm ³)	1.178	1.245	1.242
F(000)	1544	5720	1398
GOF	1.066	1.041	1.092
R1, wR2 ($I > 2\sigma(I)$)	0.0576, 0.1170	0.0645, 0.1459	0.0572, 0.1482
R1, wR2 (all data)	0.0832, 0.1272	0.1010, 0.1627	0.0649, 0.1562

X-ray Structural Determination. All intensity data were collected with a Bruker SMART CCD diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 . Hydrogen atoms were considered in calculated positions. All nonhydrogen atoms were refined anisotropically. Crystals of **3**, **6**, and **8** suitable for X-ray analysis were obtained from THF/*n*-hexane (1:1), toluene, and *n*-hexane at room temperature, respectively (Table 1).

RESULTS AND DISCUSSION

Synthesis and Characterization. The stable aluminum hydroxide $\text{LAl}(\text{OH})[\text{C}(\text{Ph})\text{CH}(\text{Ph})]$ (**1**) was prepared in high yield by controlled hydrolysis of $\text{LAl}(\eta^2\text{-C}_2\text{Ph}_2)$ ($\text{L} = \text{HC}[(\text{CMe})\text{(NAr)}]_2$, Ar = 2,6-*i*Pr₂C₆H₃) in diethyl ether. A singlet at δ 0.65 ppm in the ^1H NMR spectrum of **1** and a broad absorption centered at 3482 cm^{-1} in the IR spectrum indicated the formation of the aluminum hydroxide.^{4a,11a,15}

Reaction of $\text{LAl}(\text{OH})[\text{C}(\text{Ph})\text{CH}(\text{Ph})]$ with yttrium trialkyl $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ in *n*-hexane at 0°C yielded the oxo-bridged heterobimetallic yttrium dialkyl **2** in moderate yield (Scheme 1). Complex **2** is stable at room temperature under an inert atmosphere but crystals of **2** were gradually decomposed above 40°C in several hours. Complex **2** has been characterized by ^1H , ^{13}C NMR, IR spectroscopic methods, and elemental analysis. The methylene hydrogen atoms of $\text{Y}-\text{CH}_2\text{SiMe}_3$ resonate at δ –0.90 ppm in the proton NMR spectrum, which is slightly high-field shifted in comparison with that of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (δ –0.70 ppm). It has been demonstrated that monoligated lanthanide dialkyls could be used for the generation of highly active cationic alkyl species. However, our attempts to prepare well-defined cationic yttrium monoalkyl species from **2** with 1 equiv of $[\text{HNMe}_3][\text{BPh}_4]$ or $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ were unsuccessful.

As the thermal stability of **2** is not satisfactory for further investigation its chemistry, it is expected that the introduction of suitable ligand frameworks would modify the properties of this class of bimetallic complexes. As a continuation of our investigation on the bulky pyrrolylaldiminato ligand $[\text{NN}]\text{H}$ ($[2\text{-(ArN}=\text{CH)-5-}t\text{BuC}_4\text{H}_2\text{NH}]$) in rare earth metal chemistry,^{13,16} the new lanthanide dialkyls incorporating this ligand have been prepared as precursors for the preparation of Al–O–Ln bimetallic complexes. Thus, reaction of $[\text{NN}]\text{H}$ with 1 equiv of $\text{Ln}(\text{CH}_2\text{SiMe}_3)_3\text{(THF)}_n$ (Ln = Y, $n = 2$; Ln = Sm, $n = 3$) in *n*-hexane at room

Scheme 1. Synthesis of 1–6

Figure 1. ORTEP drawing of **3** with thermal ellipsoids at 30% probability. Hydrogen atoms and *i*Pr groups on aryl have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Y1–N2 2.391(3), Y1–O2 2.394(2), Y1–C22 2.412(3), Y1–C26 2.436(3), Y1–N1 2.529(2), Y1–O1 2.534(2), N2–Y1–O2 148.95(8), N2–Y1–C22 99.81(10), O2–Y1–C22 89.72(9), O2–Y1–C26 86.80(10), C22–Y1–C26 100.35(11), N2–Y1–N1 71.71(8), O2–Y1–O1 91.94(7), C22–Y1–O1 178.25(9).

temperature yielded the expected monoligated dialkyls [NN]Ln(CH₂SiMe₃)₂(THF)₂ (Ln = Y (**3**), Sm (**4**)). Compounds **3** and **4** have been fully characterized by multiple NMR spectroscopy and elemental analysis. The methylene hydrogen resonance (δ –0.19 ppm) of **3** falls in the typical range for this type of yttrium alkyls.

The molecular structure of **3** has been determined by an X-ray single-crystal analysis, which is shown in Figure 1 with selected bond parameters. Complex **3** is monomeric and the yttrium atom is six-coordinate with two nitrogen atoms, two THF molecules, and two CH₂SiMe₃ groups. The geometry around the yttrium atom can be best described as a slightly distorted octahedron as indicated by the almost linear O1–Y1–C22 angle (178.25(9)°). The O1–Y1 (2.534(2) Å) bond length is longer (ca. 0.14 Å)

Scheme 2. Synthesis of **7** and **8**

than that of O2–Y1 (2.394(2) Å). The Y1–C22 and Y1–C26 bond lengths (2.412(3) and 2.436(3) Å) are within the reported range for yttrium alkyls.¹⁷ The pyrrolide ligand adopts an η^2 coordination with N–Y–N angle of 71.71(8)°, which is comparable to those found in the known pyrrolide yttrium complexes.^{13,16}

The oxo-bridged heterobimetallic monoalkyls **5** and **6** can be obtained in high yields by reaction of **1** with 1 equiv of the pyrrolide dialkyls **3** and **4**. Alternatively, **5** can be prepared by the reaction of **2** with [NN]H. In the ¹H NMR spectrum of **5**, the methylene proton resonances for the CH₂SiMe₃ group can be found at δ –0.90 and 0.06 ppm (²J_{HH} = 11.2 Hz, ³J_{YH} = 3.2 and 4.0 Hz). Reactions of **5** and **6** with 1 equiv of isopropanol afforded the corresponding heterobimetallic alkoxyl complexes **7** and **8**, respectively, in good yields as shown in Scheme 2. The ¹H NMR spectrum of **7** displays a new septet centered at δ 4.61 ppm, the typical resonance for OCHMe₂ group.¹⁸ The ¹H NMR spectra of the samarium complexes **4**, **6**, and **8** display abnormal broad resonances due to their paramagnetic nature.

The molecular structures of the oxo-bridged samarium–aluminum bimetallic complexes **6** and **8** have been determined by X-ray single-crystal analysis, which are shown in Figures 2 and 3. The samarium centers in **6** and **8** are five-coordinate and can be best described as a distorted square-pyramidal geometry. The central oxygen atom links the samarium and aluminum atoms with an approximate linear Sm–O–Al angle (178.2(2)° in **6**, 174.2(2)° in **8**). The Sm1–O1 bond distances of 2.101(3) Å in **6** and 2.140(4) Å in **8** are comparable to those observed in [(C₅Me₅)₂Sm]₂(μ -O) (2.094(1) Å),¹⁹ [(C₅Me₄iPr)₂Sm]₂(μ -O) (2.116(3) Å) and

Figure 2. ORTEP drawing of **6** with thermal ellipsoids at 30% probability. Hydrogen atoms and *i*Pr groups on aryl have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Sm1–O1 2.101(3), Sm1–N2 2.424(4), Sm1–O2 2.454(3), Sm1–C22 2.473(6), Sm1–N1 2.588(4), Al1–O1 1.711(4), Al1–N3 1.917(5), Al1–N4 1.930(5), Al1–C59 1.991(5), O1–Sm1–N2 109.52(14), O1–Sm1–O2 90.20(13), O1–Sm1–C22 121.26(16), N2–Sm1–C22 103.27(16), O2–Sm1–C22 85.70(15), O1–Sm1–N1 130.93(14), N2–Sm1–N1 69.56(14), O1–Al1–N3 111.5(2), O1–Al1–N4 109.20(18), N3–Al1–N4 94.9(2), O1–Al1–C59 112.4(2), Al1–O1–Sm1 178.2(2).

Figure 3. ORTEP drawing of **8** with thermal ellipsoids at 30% probability. Hydrogen atoms and *i*Pr groups on aryl have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Sm1–O1 2.140(4), Sm1–O2 2.442(3), Sm1–O3 2.095(3), Sm1–N4 2.474(4), Sm1–N3 2.634(5), Al1–O1 1.697(4), Al1–N2 1.938(4), Al1–N1 1.944(4), Al1–C36 2.011(5), O3–Sm1–O1 118.23(14), O3–Sm1–O2 88.58(12), O1–Sm1–O2 95.41(13), O3–Sm1–N4 99.93(13), O1–Sm1–N4 109.88(13), O2–Sm1–N4 144.72(14), O3–Sm1–N3 107.96(14), O1–Sm1–N3 132.88(12), O2–Sm1–N3 76.17(14), N4–Sm1–N3 68.62(13), O1–Al1–N2 112.76(18), O1–Al1–N1 108.98(19), N2–Al1–N1 93.63(17), O1–Al1–C36 116.3(2), N2–Al1–C36 110.8(2), N1–Al1–C36 112.18(18), Al1–O1–Sm1 174.2(2).

$[(C_5Me_5)_2Sm(NC_5H_5)]_2(\mu-O)$ (2.151(2) Å).²⁰ The Al1–O1 bond distances of 1.711(4) Å in **6** and 1.697(4) Å in **8** fall in the range of the values found in known oxo-bridged heterobimetallic

Table 2. Polymerization of *rac*-Lactide with **2**, **3**, **5**, **7**, and **8**^a

entry	cat.	time (h)	[LA]/[Cat]	additive	conv (%)	M_n (10 ⁴)	PDI
1	2	15	125	none	low	n.d.	n.d.
2	2	5	125	HMDS	98	2.23	1.85
3	3	15	125	none	69	bimodal	bimodal
4	3	5	125	HMDS	100	4.18	1.71
5	5	5	125	none	98	1.41	1.95
6	5	15	250	none	45	n.d.	n.d.
7	5	1.5	125	HMDS	98	0.94	2.11
8	7	0.5	500	none	99	2.78	2.32
9	8	0.5	125	none	99	1.92	1.63
10	8	0.5	250	none	99	1.42	2.16
11	8	0.5	500	none	99	1.60	1.70
12	8	0.5	1000	none	99	4.82	1.60
13	8	1.0	2000	none	91	6.91	1.72

^a General conditions: 20 °C, 15 mL of toluene, [Cat] = 0.0013 mol/L; HMDS = 1,1,1,3,3,3-hexamethyldisilazane (0.0065 mol/L); the conversions were determined by the ¹H NMR spectra; the values of PDI were obtained by GPC calibrated with standard polystyrene sample; n. d. = not determined.

aluminum–lanthanide species (1.690(6) to 1.766(6) Å).⁵ The Sm1–O3 bond distance of 2.095(3) Å in **8** is comparable to those reported for samarium alkoxyl complexes.²¹ Compounds **6** and **8** represent the first structurally characterized oxo-bridged Al–Ln bimetallic rare earth alkyls and alkoxides. The existence of the Ln–CR₃ and Ln–OR in these complexes may allow to investigate the insertion and σ -bond metathesis chemistry of these complexes and apply these complexes to polymerization reactions.

Ring-Opening Polymerization (ROP) of *rac*-Lactide. For comparison, the mononuclear aluminum and yttrium complexes **1** and **3** were examined as initiators for the ROP of lactide in the first place. The aluminum hydroxide **1** showed very low catalytic activity within the temperature range from 25 to 70 °C while the yttrium dialkyl complex **3** is modestly active for the ROP reaction with ca. 69% conversion in 15 h at room temperature as shown in Table 2 (entry 3). The results for the polymerization reactions with the bimetallic alkyl complexes **2** and **5** are given in Table 2 (entries 1, 5, and 6). Yttrium dialkyl **2** exhibits low activity at ambient temperature, whereas yttrium monoalkyl **5** bearing the pyrrolide NN ligand shows relatively high reactivity with the formation of low molecular weight polylactides at the lactide to initiator molar ratio of 125. However, the increase of the molar ratio to 250 led to only ca. 45% conversion under the same conditions.

The catalytic activities of the bimetallic complexes could be improved by adding 1,1,1,3,3,3-hexamethyldisilazane (HMDS) as a chain transfer agent. The results for the polymerization reactions with **2**, **3**, or **5** in the presence of HMDS are summarized in Table 2 (entries 2, 4, and 7). The substantial improvements for the polymerization activity have been achieved for dialkyl complexes **2** and **3**. The addition of HMDS into the polymerization systems may result in the activation of lactide via the formation of the O···H–N hydrogen bond between the lactide carbonyl oxygen atom and the HMDS hydrogen atom or elimination of SiMe₄ to give the corresponding rare earth metal amides. In the latter case, the lanthanide amide group normally shows relatively high nucleophilicity to lactide compared to lanthanide alkyl groups.²²

Metal alkoxides have been widely used for the ROP of lactides and, in general, display a good activity and well-controlled polymerization behaviors.^{18c,23} Thus, bimetallic alkoxides **7** and **8** were employed for the polymerization reactions. The results are summarized in Table 2 (entries 8–13). As expected, **7** and **8** are highly active initiators for the ROP reactions in toluene at room temperature. Almost quantitative conversions (99%) with **7** and **8** have been observed in 30 min for the monomer-to-metal molar ratio at 500. Furthermore, polylactides obtained with **8** exhibits relatively narrow molecular weight distribution (PDI = 1.70, entry 11). Therefore, the polymerization reactions of **8** were further investigated by the increase of monomer-to-metal molar ratio (Table 2, entries 9–13). As can be seen from Table 2, complex **8** is extremely active for the ROP of rac-lactide. With increase of the molar ratio below 1000, almost complete conversions were observed in 30 min and the high conversion (91%) in 1 h was found even at the molar ratio of 2000. As far as we known, no well-defined lanthanide alkoxides have been reported to show such a high conversion at the high molar ratio at room temperature.^{18b,24} The only comparable example is an alkoxide-bridged bis(amidinate) ytterbium complex reported by Shen in 2009,^{24a} which can promote a complete conversion of 1500 equiv of L-lactide in 10 min at 100 °C. However, at the molar ratio of 2000, the conversion of the monomer with the ytterbium complex was significantly dropped to no more than 29%. No comparable aluminum alkoxides have been known to show such high activity.⁷ For **8**, with the increase of monomer-to-metal molar ratio, the molecular weights (M_n) are not increased accordingly within the ratio of 500 but noticeably increased at high molar ratios. For all of these catalysts, atactic polymers were produced based on the NMR analysis.

On the basis of the polymerization results, it is postulated that the aluminum center may not be directly involved in the polymerization reactions as indicated by the very low activity of the aluminum hydroxide **1** and increased polymerization activity with the Ln–OiPr complexes. However, the enhanced activity of the lanthanide center displayed by **8** may be largely related to the unique electronic properties of the Al–O ligand.

CONCLUSIONS

The oxo-bridged heterobimetallic aluminum–lanthanide complexes have been synthesized and characterized. The oxo-bridged bimetallic complexes feature an almost linear Al–O–Ln geometry. The catalytic behaviors of the complexes for rac-lactide polymerization were investigated, in which heterobimetallic alkoxyl complex **8** is a highly active catalyst for ring-opening polymerization of rac-lactide. The high activity observed with the bimetallic alkoxides encourages us to design new bimetallic complexes for realization of stereospecific polymerization of lactides.

ASSOCIATED CONTENT

S Supporting Information. CIF files for **3**, **6** and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: cmcui@nankai.edu.cn.

ACKNOWLEDGMENT

We are grateful to the Natural National Science Foundation of China (20972074 and 20725205). H.W.R. thanks the Deutsche Forschungsgemeinschaft for support of this work.

REFERENCES

- (1) Edelmann, F. T.; Freckmann, D. M. M.; Schumann, H. *Chem. Rev.* **2002**, *102*, 1851–1896.
- (2) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons, Inc.: Singapore, 1999.
- (3) Selected references: (a) Fischbach, A.; Meermann, C.; Eickerling, G.; Scherer, W.; Anwender, R. *Macromolecules* **2006**, *39*, 6811–6816. (b) Dietrich, H. M.; Schuster, O.; Törnroos, K. W.; Anwender, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 4858–4863. (c) Bambirra, S.; Bouwkamp, M. W.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2004**, *126*, 9182–9183. (d) Yasuda, H.; Ihara, E. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1745–1767. (e) Yasuda, H. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1955–1959.
- (4) Leading references: (a) Yang, Y.; Schulz, T.; John, M.; Yang, Z.; Jiménez-Pérez, V. M.; Roesky, H. W.; Gurubasavaraj, P. M.; Stalke, D.; Ye, H. *Organometallics* **2008**, *27*, 769–777. (b) Nikiforov, G. B.; Roesky, H. W.; Schulz, T.; Stalke, D.; Witt, M. *Inorg. Chem.* **2008**, *47*, 6435–6443. (c) Gurubasavaraj, P. M.; Roesky, H. W.; Nekoueishahraki, B.; Pal, A.; Herbst-Irmer, R. *Inorg. Chem.* **2008**, *47*, 5324–5331. (d) Mandal, S. K.; Gurubasavaraj, P. M.; Roesky, H. W.; Oswald, R. B.; Magull, J.; Ringe, A. *Inorg. Chem.* **2007**, *46*, 7594–7600. (e) Gurubasavaraj, P. M.; Mandal, S. K.; Roesky, H. W.; Oswald, R. B.; Pal, A.; Noltemeyer, M. *Inorg. Chem.* **2007**, *46*, 1056–1061. (f) Bai, G.; Singh, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2005**, *127*, 3449–3455.
- (5) Chai, J.; Jancik, V.; Singh, S.; Zhu, H.; He, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hosmane, N. S. *J. Am. Chem. Soc.* **2005**, *127*, 7521–7528.
- (6) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147–6176.
- (7) For leading references on aluminum catalysts, see: (a) Du, H.; Velders, A. H.; Dijkstra, P. J.; Zhong, Z.; Chen, X.; Feijen, J. *Macromolecules* **2009**, *42*, 1058–1066. (b) Dagorne, S.; Le Bideau, F.; Welter, R.; Bellemin-Lapponnaz, S.; Maise-Francois, A. *Chem.—Eur. J.* **2007**, *13*, 3202–3217. (c) Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 2688–2689. (d) Majerska, K.; Duda, A. *J. Am. Chem. Soc.* **2004**, *126*, 1026–1027. (f) Nomura, N.; Ishii, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, *124*, 5938–5939.
- (8) For recent references on lanthanide catalysts, see: (a) Zhang, Z.; Xu, X.; Li, W.; Yao, Y.; Zhang, Y.; Shen, Q.; Luo, Y. *Inorg. Chem.* **2009**, *48*, 5715–5724. (b) Broderick, E. M.; Diaconescu, P. L. *Inorg. Chem.* **2009**, *48*, 4701–4706. (c) Binda, P. I.; Delbridge, E. E.; Abrahamson, H. B.; Skelton, B. W. *Dalton Trans.* **2009**, 2777–2787. (d) Peng, H.; Zhang, Z.; Qi, R.; Yao, Y.; Zhang, Y.; Shen, Q.; Cheng, Y. *Inorg. Chem.* **2008**, *47*, 9828–9835. (e) Ma, H.; Spaniol, T. P.; Okuda, J. *Inorg. Chem.* **2008**, *47*, 3328–3339. (f) Sánchez-Barba, L. F.; Hughes, D. L.; Humphrey, S. M.; Bochmann, M. *Organometallics* **2005**, *24*, 3792–3799.
- (9) Stanford, M. J.; Dove, A. P. *Chem. Soc. Rev.* **2010**, *39*, 486–494.
- (10) (a) Sarish, S. P.; Nembenna, S.; Roesky, H. W.; Ott, H.; Pal, A.; Stalke, D.; Dutta, S.; Pati, S. K. *Angew. Chem., Int. Ed.* **2009**, *48*, 8740–8742. (b) Nekoueishahraki, B.; Jana, A.; Roesky, H. W.; Mishra, L.; Stern, D.; Stalke, D. *Organometallics* **2009**, *28*, 5733–5738. (c) Singh, S.; Chai, J.; Pal, A.; Jancik, V.; Roesky, H. W.; Herbst-Irmer, R. *Chem. Commun.* **2007**, 4934–4936. (d) Nembenna, S.; Roesky, H. W.; Mandal, S. K.; Oswald, R. B.; Pal, A.; Herbst-Irmer, R.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2006**, *128*, 13056–13057.
- (11) (a) Li, X.; Duan, L.; Song, H.; Ni, C.; Cui, C. *Organometallics* **2006**, *25*, 5665–5667. (b) Jancik, V.; Pineda, L. W.; Pinkas, J.; Roesky, H. W.; Neculai, D.; Neculai, A. M.; Herbst-Irmer, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 2142–2145. (c) Bai, G.; Roesky, H. W.; Li, J.; Noltemeyer, M.; Schmidt, H.-G. *Angew. Chem., Int. Ed.* **2003**, *42*, 5502–5506. (d) Bai, G.;

Peng, Y.; Roesky, H. W.; Li, J.; Schmidt, H.-G.; Noltemeyer, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1132–1135.

(12) Cui, C.; Köpke, S.; Herbst-Irmer, R.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Wrackmeyer, B. *J. Am. Chem. Soc.* **2001**, *123*, 9091–9098.

(13) Cui, C.; Shafir, A.; Reeder, C. L.; Arnold, J. *Organometallics* **2003**, *22*, 3357–3359.

(14) Hultsch, K. C.; Voth, P.; Beckerle, K.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 228–243.

(15) Zhu, H.; Chai, J.; Jancik, V.; Roesky, H. W.; Merrill, W. A.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 10170–10171.

(16) Hao, J.; Song, H.; Cui, C. *Organometallics* **2009**, *28*, 3100–3104.

(17) Yang, Y.; Li, S.; Cui, D.; Chen, X.; Jing, X. *Organometallics* **2007**, *26*, 671–678.

(18) (a) Platel, R. H.; White, A. J. P.; Williams, C. K. *Chem. Commun.* **2009**, 4115–4117. (b) Ajellal, N.; Lyubov, D. M.; Sinenkov, M. A.; Fukin, G. K.; Cherkasov, A. V.; Thomas, C. M.; Carpentier, J.-F.; Trifonov, A. A. *Chem.—Eur. J.* **2008**, *14*, 5440–5448. (c) Amgoune, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Chem.—Eur. J.* **2006**, *12*, 169–179.

(19) Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405–409.

(20) Evans, W. J.; Davis, B. L.; Nyce, G. W.; Perotti, J. M.; Ziller, J. W. *J. Organomet. Chem.* **2003**, *677*, 89–95.

(21) (a) Domingos, A.; Lopes, I.; Waerenborgh, J. C.; Marques, N.; Lin, G. Y.; Zhang, X. W.; Takats, J.; McDonald, R.; Hillier, A. C.; Sella, A.; Elsegood, M. R. J.; Day, V. W. *Inorg. Chem.* **2007**, *46*, 9415–9424. (b) Evans, W. J.; Champagne, T. M.; Ziller, J. W.; Kaltsoyannis, N. *J. Am. Chem. Soc.* **2006**, *128*, 16178–16189. (c) Barbier-Baudry, D.; Heiner, S.; Kubicki, M. M.; Vigier, E.; Visseaux, M.; Hafid, A. *Organometallics* **2001**, *20*, 4207–4210.

(22) (a) Chuma, A.; Horn, H. W.; Swope, W. C.; Pratt, R. C.; Zhang, L.; Lohmeijer, B. G. G.; Wade, C. G.; Waymouth, R. M.; Hedrick, J. L.; Rice, J. E. *J. Am. Chem. Soc.* **2008**, *130*, 6749–6754. (b) Lu, H.; Cheng, J. *J. Am. Chem. Soc.* **2007**, *129*, 14114–14115.

(23) (a) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889–899. (b) Giesbrecht, G. R.; Whitener, G. D.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2001**, 923–927. (c) Chamberlain, B. M.; Jazdzewski, B. A.; Pink, M.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **2000**, *33*, 3970–3977. (d) Chamberlain, B. M.; Sun, Y.; Hagadorn, J. R.; Hemmesch, E. W.; Young, V. G., Jr.; Pink, M.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **1999**, *32*, 2400–2402.

(24) (a) Wang, J.; Yao, Y.; Zhang, Y.; Shen, Q. *Inorg. Chem.* **2009**, *48*, 744–751. (b) Platel, R. H.; White, A. J. P.; Williams, C. K. *Chem. Commun.* **2009**, 4115–4117. (c) Save, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 2591–2603. (d) Simic, V.; Spassky, N.; Hubert-Pfalzgraf, L. G. *Macromolecules* **1997**, *30*, 7338–7340. (e) Stevels, W. M.; Ankoné, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 6132–6138.