Bimetallic Rare Earth Alkyl Complexes Bearing Bridged Amidinate Ligands: Synthesis and Activity for *L*-Lactide Polymerization

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Four novel bridged-amidines H_2L {1,4-$R^1[C(=NR^2)(NHR^2)]_2$ [$R^1=C_6H_4$, $R^2=2,6\text{-}^iPr_2C_6H_3$ (H_2L^1); $R^1=C_6H_4$, $R^2=2,6\text{-}Me_2C_6H_3$ (H_2L^2); $R^1=C_6H_{10}$, $R^2=2,6\text{-}^iPr_2C_6H_3$ (H_2L^3); $R^1=C_6H_{10}$, $R^2=2,6\text{-}Me_2C_6H_3$ (H_2L^4)]} were synthesized in 65%—78% isolated yields by the condensation reaction of dicarboxylic acid with four equimolar amounts of amines in the presence of PPSE at 180 ℃. Alkane elimination reaction of $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln=Y, Lu) with 0.5 equiv. of amidine in THF at room temperature afforded the corresponding bimetallic rare earth alkyl complexes $(THF)(Me_3SiCH_2)_2LnL^1Ln(CH_2SiMe_3)_2(THF)$ [Ln = Y (**1**), Lu (**2**)], $(THF)(Me_3SiCH_2)_2LnL^2Ln(CH_2SiMe_3)_2(THF)$ [Ln=Y (**3**), Lu (**4**)], $(THF)(Me_3SiCH_2)_2YL^3Y(CH_2SiMe_3)_2(THF)$ (**5**), $(THF)(Me_3SiCH_2)_2YL^4Y(CH_2SiMe_3)_2(THF)$ (**6**) in 72%—80% isolated yields. These neutral complexes showed activity towards *L*-lactide polymerization in toluene at 70 ℃ to give high molecular weight ($M>10^4$) and narrow molecular weight distribution ($M_w/M_n\leqslant 1.40$) polymers.

Keywords　rare earths, bridged amidinate ligand, synthesis, ring-opening polymerization

Introduction

Over the past decade organo rare earth metal bis(alkyl) complexes with a general formula $LLnR_2(S)_x$ (L=monoanionic ancillary ligand, Ln=rare earth metal, R=alkyl, S=coordinated solvent, x=coordinated solvent number) have attracted increasing interest and made spectacular progress as catalyst precursors in organic transformation and polymerization.[1-5] However, such complexes are usually rather difficult to characterize and are often much less thermally stable compared to rare earth metal mono(alkyl) complexes. Therefore, most of rare earth metal bis(alkyl) complexes are mononuclear, and should be stabilized by cyclopentadienyl derivatives,[6-19] or sterically bulky non-cyclopentadienyl ancillary ligands such as β-diketiminates,[20-25] amidinates,[26-35] anilido-imine,[36,37] *etc.* Very recently, it was found that, in particular in the field of organometallic chemistry of transition metals, multinuclear metal complexes could possess unique or more efficient homogeneous catalytic processes than mononuclear species, benefiting from cooperative effects between proximate functional groups or adjacent active metal centers.[38,39] Although Marks and co-workers also described that the bridged-Cp binuclear rare earth metal amide complexes showed much more efficient catalytic activity towards olefin intramolecular hydroamination/cyclization,[40,41] in contrast, little is known about multinuclear organo rare earth metal alkyl complexes to date.[42] Herein, we would like to report the preparation of bimetallic rare earth alkyl complexes supported by bridged-amidinates, as well as their performance as initiators for *L*-lactide polymerization.

Results and discussion

Synthesis and characterization of the bridged amidines H_2L^{1-4}

According to procedures reported in the literature, in some cases with little modification, we reported previously that carboxylic acids reacted with 2 equiv. of amines in the presence of polyphosphoric acid trimethylsilyl ester (PPSE) at 180 ℃ could afford a variety of amidines in good isolated yields.[35,43] In this work, instead of monocarboxylic acids, dicarboxylic acids were reacted with four equimolar amounts of

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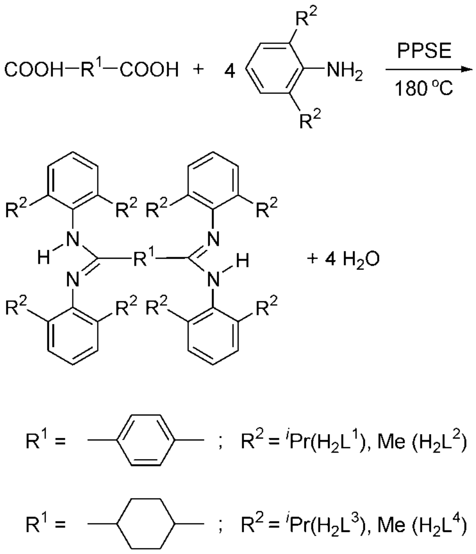
amines in the presence of PPSE at 180 ℃ to give the bridged amidines $H_2L^{1\text{-}4}$ as off-white/pale-green powders after extractive work-up and solvent evaporation (Scheme 1). Recrystallization from hot toluene or THF provided the pure bridged amidines as white/pale-green solids or microcrystals, which were characterized by NMR spectroscopy, HRMS, FT-IR spectroscopy, and elemental analysis. ^{1}H NMR spectra of $H_2L^{1\text{-}4}$ indicate that the N—H proton resonances appear as a broad singlet between δ 5.2 and 5.7.

Scheme 1



Synthesis and characterization of the bimetallic rare earth alkyl complexes

To obtain neutral rare earth metal bis(alkyl) complexes, it has proven that an appropriate metal/ligand combination is rather critical and alkane elimination reaction is a straightforward strategy. NMR monitoring technique showed the reaction of $Y(CH_2SiMe_3)_3(THF)_2$ with 0.5 equiv. of H_2L^1 in benzene-d_6 at room temperature occurred smoothly, affording $(THF)_x(Me_3SiCH_2)_2$-$YL^1Y(CH_2SiMe_3)_2(THF)_x$ as a neat product in several hours, with the elimination of tetramethylsilane. No ligand redistribution was observed. On a preparative scale, treatment of $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln=Y, Lu) with 0.5 equiv. of the amidines H_2L in THF at room temperature, after workup, gave complexes **1**—**6** in 72%—80% yields (Scheme 2).

Complexes **1**—**6** are all air- and moisture-sensitive, soluble in THF, toluene, and lightly soluble in aliphatic solvents such as hexane and pentane. They were characterized by elemental analysis, FT-IR, and NMR spectroscopy. Although some of these complexes could be obtained in the form of single crystals, the attempts to authenticate their single crystal structures were unsuccessful due to their extremely fast desolvation.

Room-temperature ^{1}H NMR spectra of **1**, **3**, **5** and **6** (yttrium complexes) in C_6D_6 show an AB spin for the methylene resonances of Y-C**H**$_2$SiMe$_3$. The methylene resonances for these complexes were found from δ −0.2 to −0.4 (^{1}H, d, $J_{\text{Y-H}}$=2.7—3.0 Hz), which are identical to the equivalent resonances in the related mononuclear analogues.[27,28,35] In **1**, **3** and **5**, **6**, the main difference is the linked-bridge at the carbon atom of ligating NCN moiety (phenyl group for **1**, **3** and cyclohexyl group for **5**, **6**), however, all of the methylene resonances of Y-C**H**$_2$SiMe$_3$ appear around δ 40 in ^{13}C NMR spectra, suggesting a similar electronic yttrium environment. In the cases of lutetium complexes **2** and **4**, the methylene protons of Lu-C**H**$_2$SiMe$_3$ display sharp singlet resonances at −0.40 and −0.43 in ^{1}H NMR spectra, respectively. Restricted rotation about the N-C$_{\text{aryl}}$ bonds gives rise to two separate doublets for the isopropyl methyl groups in the related complexes.

L-Lactide polymerization initiated by the bimetallic rare earth alkyl complexes

To investigate the reactivity of the bimetallic rare earth alkyl complexes, these complexes were employed as initiators for *L*-lactide polymerization. Some selected mononuclear amidinate rare earth metal bis(alkyl) complexes were also involved in this experiment to reveal whether the bimetallic species could exhibit cooperative effect. The preliminary polymerization results are summarized in Table 1.

All these neutral bimetallic rare earth alkyl complexes showed activity towards *L*-lactide polymerization, and the conversions exceeded 76% at 70 ℃ for 30 min in toluene in the case of [M]/[I]=100 (molar ratio). The bimetallic complexes showed very similar polymeriza-

Scheme 2

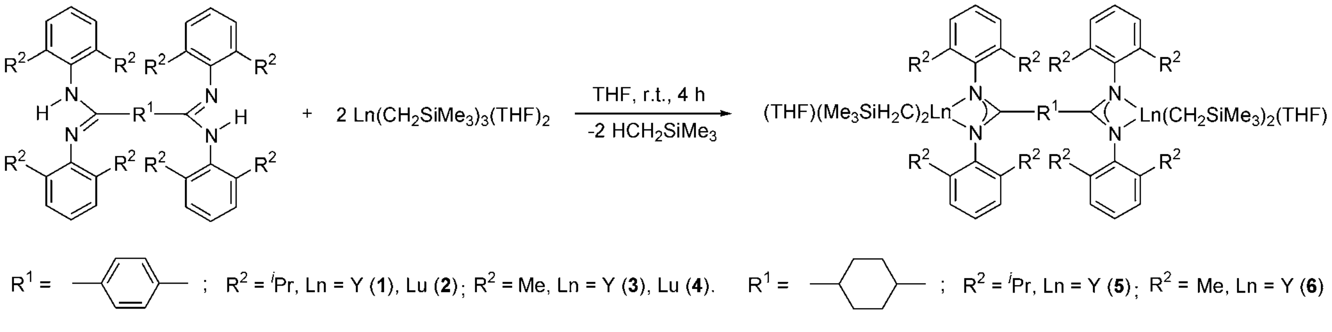
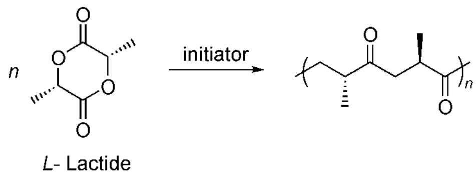


Table 1 *L*-Lactide polymerization with rare earth alkyl amidinate complexes[a]



Run	Initiator	Yield[b]/%	$M_{n,calcd}$[c]$\times 10^{-4}$	$M_{n,obsd}$[d]$\times 10^{-4}$	M_w/M_n[d]
1	**1**	91	0.33	2.28	1.39
2	**2**	89	0.32	2.41	1.33
3	**3**	78	0.28	1.85	1.30
4	**4**	82	0.30	1.96	1.35
5	**5**	86	0.31	2.08	1.39
6	**6**	76	0.27	1.38	1.40
7	$[PhC(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2]Y(CH_2SiMe_3)_2(THF)$	89	0.64	2.33	1.26
8	$[CyC(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2]Y(CH_2SiMe_3)_2(THF)$	91	0.66	3.36	1.20
9	$[CyC(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2]Lu(CH_2SiMe_3)_2(THF)$	100	0.72	4.71	1.25

[a] Polymerization conditions: [L-LA]/[Ln]=100, [L-LA]=0.5 mol•L^{-1}, in toluene, t=30 min, 70 ℃; [b] Isolated yields of PLA; [c] M_n of PLA calculated from $M_{n,calcd}=144\times([LA]/4[Ln])\times$yield (LA), except for runs 7—9, in which $M_{n,calcd}=144\times([LA]/2[Ln])\times$yield (LA); [d] Determined by GPC at 40 ℃ in THF relative to polystyrene standards; corrected by the Mark-Houwink equation [$M_{n,obsd}=0.58M_n$ (GPC)].[48]

tion activity compared with the mononuclear complexes. Although each bimetallic complex possesses two center metals, GPC curves of the resulting polymers were all unimodal with quite narrow molecular weight distributions ($M_w/M_n \leqslant 1.40$), indicative of single-site catalyst behavior as observed in other rare earth metal bis(alkyl) catalyst systems.[21,35,44,45] However, the resulting molecular weight distributions ($M_w/M_n \leqslant 1.40$) were slightly broader than those from mononuclear complexes ($M_w/M_n \leqslant 1.26$).[35] The observed molecular weights of M_n are much greater than the calculated molecular weights, suggesting rather low initiation efficiency with these initiators. Taking the activity and M_n into consideration, each center metal in the bimetallic complexes seems to be independent and has similar initiation capability. Cooperative effect has not been observed in this polymerization system. Different to the mononuclear amidinate rare earth metal bis(alkyl) complexes, with which the effective ionic radii of center metals (Y^{3+}=1.040 Å, Lu^{3+}=1.001 Å)[46] could affect the polymerization activity, the central metals in the bimetallic amidinate complexes showed little influence on the polymerization activity (runs 1 and 2, 3 and 4). However, the polymerization activity is somewhat dependent on the amidinate ligands. For example, employing the 1,4-phenylene group as a bridge, the initiation activity of the resulting complexes increased with the steric hindrance of the amidinates (runs 1 and 3). However, the effect of the “bridge” in these amidinate ligands on the polymerization is not so significant (runs 1 and 5).

Conclusion

In summary, a series of bimetallic rare earth alkyl complexes bearing bridged-amidinate ligands were prepared by alkane elimination reaction. These neutral bimetallic alkyl complexes were active for *L*-lactide polymerization to give high molecular weight ($M_n > 10^4$) and narrow molecular weight distribution ($M_w/M_n \leqslant 1.40$) polymers. Cooperative effect was not observed under current polymerization conditions.

Experimental

General considerations

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques and a glovebox. Solvents (toluene, hexane, and THF) were distilled from sodium/benzophenone ketyl, degassed by the freeze-pump-thaw method, and dried over fresh Na chips in the glovebox. Dichloromethane was dried by stirring with CaH_2, and distilled before use. Anhydrous $LnCl_3$ were purchased from STREM. $LiCH_2SiMe_3$ (1 mol•L^{-1} solution in pentane) was obtained from Aldrich, dried under vacuum before use. P_2O_5 was purchased from Sinopharm Chemical Reagent Co. Ltd. Hexamethyldisiloxane, 2,6-diisopropylaniline, 2,6-dimethylaniline, terephthalic acid, and 1,4-cyclohexanedicarboxylic acid were purchased from Acros, and used as received. *L*-lactide was purchased from TCI, and recrystallized from hot toluene. Deuterated solvents ($CDCl_3$, C_6D_6) were obtained from CIL. $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln=Y, Lu),[35,47] polyphosphoric acid trimethylsilyl ester (PPSE),[42] $[PhC(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2]Y(CH_2SiMe_3)_2(THF)$,[27,28] and $[CyC(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2]Ln(CH_2SiMe_3)_2(THF)$ (Ln=Y, Lu)[35] were prepared according to the literature.

Samples of organo rare earth metal complexes for

NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. NMR (^{1}H, ^{13}C) spectra were recorded on a Bruker AVANCE III spectrometer at 25 ℃. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument, quoted data are the average of at least two independent determinations. Rare earth metal analyses were carried out by complexometric titration. FT-IR spectra were recorded on a Bruker TENSOR 27 spectrometer. TOF HRMS data were obtained from a Micromass OR-TOF spectrometer. Melting points were not calibrated. Molecular weight and molecular weight distribution of the polymers were measured by PL GPC 50 at 40 ℃ using THF as eluent against polystyrene standards.

Synthesis of *p*-phenylene-bis[*N*,*N'*-bis(2,6-diisopropyl phenyl)formamidine] 1,4-$C_6H_4[C(=N\text{-}2,6\text{-}{}^iPr_2\text{-}C_6H_3)(NH\text{-}2,6\text{-}{}^iPr_2C_6H_3)]_2$ (H_2L^1)

In a Schlenk flask, P_2O_5 (9.0 g, 63.4 mmol), hexamethyldisiloxane (20 mL, 93.7 mmol), and dry dichloromethane (20 mL) were refluxed for 30 min. Then the volatiles were removed under vacuum to afford a viscous syrup PPSE. Terephthalic acid (0.62 g, 3.75 mmol) and 2,6-diisopropylaniline (3.0 mL, 15.08 mmol) were added to this viscous syrup, and the mixture was reacted at 180 ℃ for 8 h. The resulting mixture was poured into 1 mol•L^{-1} NaOH solution (150 mL) to produce an oily product, which was allowed to solidify overnight. The solid was washed with water and recrystallized from toluene to give the title compound as pale green powder. Yield 2.16 g (75%), m.p. 221.6 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.85 [d, $J=6.4$ Hz, 12H, $CH(C\mathbf{H}_3)_2$], 0.94 [d, $J=6.4$ Hz, 12H, $CH(C\mathbf{H}_3)_2$], 1.16 [d, $J=6.4$ Hz, 12H, $CH(C\mathbf{H}_3)_2$], 1.32 [d, $J=6.4$ Hz, 12H, $CH(C\mathbf{H}_3)_2$], 3.10—3.15 [m, 8H, $C\mathbf{H}(CH_3)_2$], 5.65 (s, 2H, NH), 6.95—7.23 (m, 16H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 22.4, 22.5, 24.2, 25.4 [$CH(\mathbf{C}H_3)_2$], 24.4 [$CH(\mathbf{C}H_3)_2$], 25.4 [$CH(\mathbf{C}H_3)_2$], 28.3 [$\mathbf{C}H(CH_3)_2$], 28.3, 28.6 [$\mathbf{C}H(CH_3)_2$], 122.5, 123.2, 127.7, 127.9, 133.7, 136.0, 139.2, 143.5, 145.3 (ArC), 153.4 (NCN); FT-IR (KBr) *v*: 3432 (s), 2962 (s), 2868 (m), 1618 (s), 1585 (m), 1465 (m), 1434 (m), 1384 (m), 1358 (m), 1255 (w), 1188 (w), 760 (m) cm^{-1}. Anal. calcd for $C_{56}H_{74}N_4$: C 83.74, H 9.29, N 6.98; found C 83.42, H 9.84, N 6.74. HRMS calcd for $[C_{56}H_{74}N_4]^+$ 802.5913, found 802.5938.

Synthesis of *p*-phenylene-bis[*N*,*N'*-bis(2,6-dimethylphenyl)formamidine] 1,4-$C_6H_4[C(=N\text{-}2,6\text{-}Me_2C_6H_3)\text{-}(NH\text{-}2,6\text{-}Me_2C_6H_3)]_2$ (H_2L^2)

H_2L^2 was prepared by a procedure similar to that of H_2L^1. Using terephthalic acid (0.62 g, 3.75 mmol) and 2,6-dimethylaniline (1.85 mL, 15.0 mmol), the title compound was produced as pale green powder after recrystallization from toluene. Yield 1.70 g (78%), m.p. 277.6 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.07 (s, 12H, CH_3), 2.31 (s, 12H, CH_3), 5.68 (s, 2H, NH), 6.87—7.28 (m, 16H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 17.9, 19.0 (CH_3), 123.1, 126.7, 127.6, 128.0, 128.2, 128.6, 134.8, 136.3, 136.8, 145.7 (Ar—C), 153.4 (NCN); FT-IR (KBr) *v*: 3375 (s), 2917 (m), 1630 (s), 1587 (m), 1462 (m), 1348 (m), 1205 (m), 766 (m) cm^{-1}. Anal. calcd for $C_{40}H_{42}N_4$: C 83.01, H 7.37, N 9.68; found C 83.18, H 7.65, N 9.16. HRMS calcd for $[C_{40}H_{42}N_4]^+$ 578.3409, found 578.3419.

Synthesis of *p*-cyclohexylene-bis[*N*,*N'*-bis(2,6-diisopropylphenyl)formamidine] 1,4-$C_6H_{10}[C(=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(NH\text{-}2,6\text{-}{}^iPr_2C_6H_3)]_2$ (H_2L^3)

H_2L^3 was prepared by a procedure similar to that of H_2L^1. Using 1,4-cyclohexanedicarboxylic acid (0.62 g, 3.75 mmol) and 2,6-diisopropylaniline (3.0 mL, 15.0 mmol), the title compound was produced as white powder after recrystallization from toluene. Yield 2.16 g (71%), m.p. 271.6 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.97 [d, $J=6.8$ Hz, 12H, $CH(C\mathbf{H}_3)_2$], 1.12 [d, 12H, $CH(C\mathbf{H}_3)_2$], 1.25 [d, $J=6.8$, 12H, Hz, $CH(C\mathbf{H}_3)_2$], 1.26 [d, $J=6.8$ Hz, 12H, $CH(C\mathbf{H}_3)_2$], 1.66—1.70 (m, 4H, CH_2), 1.86 (d, $J=7.2$ Hz, 4H, CH_2), 2.15 (brs, 2H, CH), 3.04—3.08 [m, 4H, $C\mathbf{H}(CH_3)_2$], 3.14—3.20 [m, 4H, $C\mathbf{H}(CH_3)_2$], 5.20 (s, 2H, NH), 6.98 (t, $J=7.6$ Hz, 2H, ArH), 7.10 (d, $J=8.0$ Hz, 8H, ArH), 7.25 (t, $J=7.6$ Hz, 2H, Ar**H**); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 22.8, 23.0, 24.1, 25.5 [$CH(\mathbf{C}H_3)_2$], 28.0, 28.1 [$\mathbf{C}H(CH_3)_2$], 30.3 (Cy-CH_2), 38.1 (Cy-CH), 122.9, 123.0, 123.8, 128.3, 132.6, 139.2, 143.7, 147.0 (Ar—C), 159.3 (NCN); FT-IR (KBr) *v*: 3365 (m), 2961 (s), 2927 (m), 2867 (m), 1632 (s), 1586 (m), 1459 (m), 1432 (m), 1385 (m), 1346 (w), 763 (m) cm^{-1}. Anal. calcd for $C_{56}H_{80}N_4$: C 83.11, H 9.96, N 6.92; found C 83.57, H 9.69, N 6.74. HRMS calcd for $[C_{56}H_{80}N_4]^+$ 808.6383, found 808.6425.

Synthesis of *p*-cyclohexylene-bis[*N*,*N'*-bis(2,6-dimethylphenyl)formamidine] 1,4-$C_6H_{10}[C(=N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(NH\text{-}2,6\text{-}Me_2C_6H_3)]_2$ (H_2L^4)

H_2L^4 was prepared by a procedure similar to that of H_2L^1. Using 1,4-cyclohexanedicarboxylic acid (0.62 g, 3.75 mmol) and 2,6-dimethylaniline (1.85 mL, 15.0 mmol), the title compound was produced as white powder after recrystallization from THF. Yield 1.4 g (65%), m.p. 340.3 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.69 (m, $J=9.5$, 4H, CH_2), 1.88—1.90 (m, $J=7.0$ Hz, 4H, CH_2), 2.07 (brs, 2H, CH), 2.18 (d, $J=4.8$ Hz, 24H, CH_3), 5.28 (s, 2H, NH), 6.85 (t, $J=7.4$ Hz, 2H, ArH), 7.02—7.05 (m, 10H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 17.8, 18.8 (CH_3), 30.7 (Cy-CH_2), 38.6 (Cy-CH), 122.5, 127.4, 128.2, 128.6, 128.9, 135.9, 136.4, 145.7 (Ar—C), 159.7 (NCN); FT-IR (KBr) *v*: 3442 (s), 2924 (m), 1641 (s), 1589 (m), 1473 (m), 1389 (w), 1222 (w), 1094 (w), 765 (m) cm^{-1}. Anal. calcd for $C_{40}H_{48}N_4$: C 82.15, H 8.27, N 9.58; found C 81.92, H 8.36, N 9.72. HRMS calcd for $[C_{40}H_{48}N_4]^+$ 584.3879, found 584.3853.

Synthesis of $(THF)(Me_3SiCH_2)_2YL^1Y(CH_2SiMe_3)_2\text{-}(THF)$ (1)

To a 30 mL of THF solution of $Y(CH_2SiMe_3)_3\text{-}(THF)_2$ (0.80 g, 1.62 mmol), was added H_2L^1 (0.65 g, 0.81 mmol) in 20 mL of THF slowly at room temperature. The mixture was stirred at room temperature for 4 h. Then the solution was concentrated under reduced pressure and cooled at －30 ℃ to afford **1** as pale green microcrystals in two crops. Yield 0.96 g (80.7%); ^{1}H NMR (400 MHz, C_6D_6) *δ*: －0.20 (d, *J*＝2.9 Hz, 8H, C**H**$_2$SiMe$_3$), 0.25 (s, 36H, SiMe$_3$), 0.80 [d, *J*＝6.8 Hz, 24H, CH(C**H**$_3$)$_2$], 1.17 (brs, 8H, *β*-THF), 1.30 [d, *J*＝6.8 Hz, 24H, CH(C**H**$_3$)$_2$], 3.40—3.47 [m, 8H, C**H**(CH$_3$)$_2$], 3.60 (brs, 8H, *α*-THF), 6.80—6.92 (m, 16H, ArH); ^{13}C NMR (100 MHz, C_6D_6) *δ*: 4.3 (TMS), 23.7 [CH(C**H**$_3$)$_2$], 25.1 (*β*-THF), 26.4, 28.4 [CH(C**H**$_3$)$_2$], 40.0 (d, *J*＝41 Hz, CH$_2$TMS), 69.9 (*α*-THF), 123.9, 125.0, 133.3, 142.4, 142.5 (Ar—C), 175.0 (NCN); FT-IR (KBr) *v*: 2963 (s), 2871 (m), 1620 (s), 1466 (m), 1358 (m), 1250 (m), 856 (m), 764 (m) cm^{-1}. Anal. calcd for $C_{80}H_{132}N_4O_2Si_4Y_2$ (1472.34): C 65.25, H 9.05, N 3.80, Y 12.08; found C 64.87, H 9.13, N 3.62, Y 11.76.

Synthesis of (THF)(Me$_3$SiCH$_2$)$_2$LuL^{1}Lu(CH$_2$SiMe$_3$)$_2$(THF) (2)

Complex **2** was prepared by a procedure similar to that of complex **1**. Using H_2L^1 (0.65 g, 0.81 mmol) and Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.94 g, 1.62 mmol), **2** was afforded as green powder. Yield 1.01 g (78.2%); ^{1}H NMR (400 MHz, C_6D_6) *δ*: －0.40 (s, 8H, C**H**$_2$TMS), 0.26 (s, 36H, CH$_2$**TMS**), 0.80 [d, *J*＝6.8 Hz, 24H, CH(C**H**$_3$)$_2$], 1.12 (brs, 8H, *β*-THF), 1.32 [d, *J*＝6.7 Hz, 24H, CH(C**H**$_3$)$_2$], 3.42—3.49 [m, 8H, C**H**(CH$_3$)$_2$], 3.61 (brs, 8H, *α*-THF), 6.83—6.89 (m, 12H, ArH); ^{13}C NMR (100 MHz, C_6D_6) *δ*: 5.7 (TMS), 25.2 [CH(**C**H$_3$)$_2$], 26.2 (*β*-THF), 27.7, 29.5 [CH(CH$_3$)$_2$], 47.6 (CH$_2$TMS), 71.8 (*α*-THF), 125.2, 126.4, 134.9, 143.7, 144.0 (Ar—C), 175.7 (NCN); FT-IR (KBr) *v*: 2963 (s), 2871 (s), 1620 (s), 1589 (s), 1458 (s), 1358 (s), 1250 (m), 856 (m), 764 (m) cm^{-1}. Anal. calcd for $C_{80}H_{132}Lu_2N_4O_2Si_4$ (1644.46): C 58.42, H 8.10, N 3.40, Lu 21.28; found C 58.91, H 7.97, N 3.24, Lu 21.03.

Synthesis of (THF)(Me$_3$SiCH$_2$)$_2$YL^{2}Y(CH$_2$SiMe$_3$)$_2$(THF) (3)

To a 30 mL of THF solution of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.677 g, 1.36 mmol), was added H_2L^2 (0.40 g, 0.68 mmol) in 20 mL of THF slowly at room temperature. After the reaction mixture was stirred at room temperature for 4 h, the solvent was removed under reduced pressure. The resulting pale yellow residue was washed with hexane (5 mL×2), and the residue was extracted by a mixture solution of THF and hexane in 1∶1 volume ratio. Then the extractant was filtrated, and the filtrate was concentrated under reduced pressure and cooled at －30 ℃ to afford **3** as pale green microcrystals. Yield 0.61 g (72%); ^{1}H NMR (400 MHz, C_6D_6) *δ*: －0.42 (d, *J*＝3.0 Hz, 8H, C**H**$_2$TMS), 0.26 (s, 36H, CH$_2$**TMS**), 0.98 (brs, 8H, *β*-THF), 2.10 (s, 24H, Ph-**Me**), 3.52 (brs, 8H, *α*-THF), 6.55, 6.79—6.85 (m, 16H, ArH); ^{13}C NMR (100 MHz, C_6D_6) *δ*: 4.4 (TMS), 19.8 (Ph-**Me**), 24.9 (*β*-THF), 40.1 (**C**H$_2$SiMe$_3$), 69.9 (*α*-THF), 123.9, 126.9, 132.3, 134.9, 145.7 (Ar—C), 173.3 (NCN); FT-IR (KBr) *v*: 2951 (s), 1627 (m), 1589 (m), 1467 (s), 1247 (m), 1200 (m), 1094 (m), 985 (m), 853 (s), 764 (s) cm^{-1}. Anal. calcd for $C_{64}H_{100}N_4O_2Si_4Y_2$ (1247.86): C 61.60, H 8.09, N 4.49, Y 14.25; found C 61.32, H 8.01, N 4.52, Y 13.88.

Synthesis of (THF)(Me$_3$SiCH$_2$)$_2$LuL^{2}Lu(CH$_2$SiMe$_3$)$_2$(THF) (4)

Complex **4** was prepared by a procedure similar to that of complex **3**. Using H_2L^2 (0.43 g, 0.73 mmol) and Lu(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.847 g, 1.46 mmol), **4** was afforded as pale yellow powder. Yield 0.77 g (74.4%); ^{1}H NMR (400 MHz, C_6D_6) *δ*: －0.43 (s, 8H, C**H**$_2$TMS), 0.25 (s, 36H, CH$_2$**TMS**), 1.01 (brs, 8H, *β*-THF), 2.11 (s, 24H, Ph-**Me**), 3.54 (brs, 8H, *α*-THF), 6.55—6.83 (m, 16H, ArH); ^{13}C NMR (100 MHz, C_6D_6) *δ*: 4.4 (TMS), 19.8 (Ph-**Me**), 24.9 (*β*-THF), 46.0 (CH$_2$SiMe$_3$), 69.9 (*α*-THF), 123.9, 126.9, 132.3, 134.9, 145.7 (Ar—C), 173.2 (NCN); FT-IR (KBr) *v*: 2951 (s), 1625 (s), 1589 (m), 1466 (s), 1392 (m), 1248 (s), 1200 (m), 1094 (m), 990 (m), 858 (s), 762 (s) cm^{-1}. Anal. calcd for $C_{64}H_{100}Lu_2N_4O_2Si_4$ (1419.98): C 54.13, H 7.11, N 3.95, Lu 24.64; found C 54.32, H 7.01, N 3.86, Lu 24.56.

Synthesis of (THF)(Me$_3$SiCH$_2$)$_2$YL^{3}Y(CH$_2$SiMe$_3$)$_2$(THF) (5)

Complex **5** was prepared by a procedure similar to that of complex **3**. Using H_2L^3 (0.497 g, 0.62 mmol) and Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.614 g, 1.24 mmol), **5** was afforded as colorless needle crystals. Yield 0.71 g (77.9%); ^{1}H NMR (400 MHz, C_6D_6) *δ*: －0.29 (d, *J*＝3.0 Hz, 8H, C**H**$_2$TMS), 0.24 (s, 36H, CH$_2$**TMS**), 0.70—0.76 (m, 4H, Cy-C**H**$_2$), 1.07 (brs, 8H, *β*-THF), 1.11 [d, *J*＝6.8 Hz, 24H, CH(C**H**$_3$)$_2$], 1.29 [d, *J*＝6.8 Hz, CH(C**H**$_3$)$_2$], 1.53 (d, 4H, Cy-C**H**$_2$), 2.08 (brs, 2H, Cy-C**H**), 3.34—3.41 [m , 8H, C**H**(CH$_3$)$_2$], 3.53 (brs, 8H, *α*-THF), 6.98—7.05 (m, 12H, Ar-**H**); FT-IR (KBr) *v*: 2963 (s), 2871 (s), 1636 (s), 1589 (m), 1458 (s), 1389 (s), 1358 (m), 1327 (m), 1250 (s), 1049 (m), 933 (m), 856 (m), 764 (m) cm^{-1}. Anal. calcd for $C_{80}H_{138}N_4O_2Si_4Y_2$ (1478.40): C 64.99, H 9.43, N 3.79, Y 12.03; found C 65.09, H 9.52, N 3.73, Y 11.75.

Synthesis of (THF)(Me$_3$SiCH$_2$)$_2$YL^{4}Y(CH$_2$SiMe$_3$)$_2$(THF) (6)

Complex **6** was prepared by a procedure similar to that of complex **3**. Using H_2L^4 (0.50 g, 0.86 mmol) and Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.85 g, 1.71 mmol), **6** was afforded as colorless needle crystals. Yield 0.60 g (76.3%); ^{1}H NMR (400 MHz, C_6D_6) *δ*: －0.38 (d, *J*＝2.7 Hz, 8H, C**H**$_2$TMS), 0.23 (s, 36H, CH$_2$**TMS**), 0.66—0.71 (m, 4H, Cy-C**H**$_2$), 1.05 (brs, 8H, *β*-THF), 1.55 (d, *J*＝7.6 Hz, 4H, Cy-C**H**$_2$), 1.79 (brs, 2H, Cy-C**H**), 2.18 (s, 24H, Ph-**Me**), 3.49 (brs, 8H, *α*-THF), 6.87 (s, 12H, ArH); ^{13}C NMR (100 MHz, C_6D_6) *δ*: 4.3 (TMS), 19.9 (Ph-**Me**), 24.8 (*β*-THF), 29.0 (Cy-CH$_2$), 38.2, 38.6 (**C**H$_2$TMS), 43.0 (Cy-**C**H), 69.8 (*α*-THF), 123.8, 132.1, 145.7 (Ar—C), 178.8 (NCN); FT-IR (KBr) *v*: 2950 (s), 1640 (s), 1590 (s), 1473 (s), 1390 (m), 1375 (m), 1249 (s), 1035 (m), 988 (m), 856 (s), 764 (m) cm^{-1}. Anal. calcd for $C_{64}H_{106}N_4O_2Si_4Y_2$ (1253.92): C 61.30, H 8.54, N 4.47, Y 14.18; found C 61.54, H 8.52, N 4.34, Y 14.32.

A typical procedure for *L*-lactide polymerization run (1, Table 1)

In a 20 mL Schleck flask, complex **1** (19 mg, 13 μmol), *L*-lactide (368 mg, 2.6 mmol), and toluene (5.2 mL) were stirred at 70 ℃ for 30 min. The polymerization was terminated by quenching with excess ethanol containing 5% aq. HCl. The polymer was collected, and dried under vacuum at 60 ℃ to constant weight (335 mg, 91%).

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