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Substituent Effects of Pyridyl-methylene Cyclopentadienyl Rare-earth Metal Complexes on Styrene Polymerization

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Electronic Supplementary Information

Abstract Salt metathesis reactions between pyridyl-methylene-cyclopentadienyl lithium salt and LnCl_3 followed by the addition of two equivalents of $\text{LiCH}_2\text{SiMe}_3$ afforded a series of constrained-geometry-configuration rare-earth metal bis(alkyl) complexes $(\text{Cp}'\text{CH}_2\text{Py})\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})_n$ ($\text{Py} = \text{C}_5\text{H}_4\text{N}$, $\text{Cp}' = \text{C}_5\text{H}_4$ (**1**), $\text{Cp}' = \text{C}_9\text{H}_6$ (**2**), $\text{Cp}' = 3\text{-Me}_3\text{Si-C}_9\text{H}_5$ (**3a**), $\text{Ln} = \text{Sc}$, $n = 0$ (**3a**), $\text{Ln} = \text{Lu}$ (**3b**), **Y** (**3c**), $n = 1$; $\text{Cp}' = 2,7\text{-(}^t\text{Bu)}_2\text{C}_{13}\text{H}_8$ (**2,7-(}^t\text{Bu)}_2\text{-Flu}**), $\text{Ln} = \text{Sc}$ (**4a**), $n = 0$, $\text{Ln} = \text{Lu}$ (**4b**), **Y** (**4c**), $n = 1$) in moderate to good yields, which were characterized by NMR spectroscopy and single-crystal X-ray diffraction (for complex **3a**). In the presence of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and Al^iBu_3 , these complexes displayed different performances towards styrene polymerization. Rare-earth metal bis(alkyl) precursors bearing Cp, Ind, and 3-Me₃Si-Ind segments exhibited very low catalytic activity to afford syndiotactic polystyrene. All electron-donating ^tBu substituted complexes **4a**, **4b**, and **4c** showed very high activity and perfect syndiotacticity (*rrrr* > 99%), producing high molecular weight polystyrene (up to 54.1×10^4) with relatively narrow molecular distribution (*PDI* = 1.28–2.49).

Keywords Polystyrene; Syndiotactic; Rare-earth metal; Constrained-geometry configuration

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INTRODUCTION

Syndiotactic polystyrene has attracted extensive attention in both academic and industrial communities, due to its excellent chemical and physical properties.^[1–7] For example, it has high melting point ($T_m \approx 270^\circ\text{C}$), fast crystallization rate, high modulus of elasticity, and low dielectric constant, and is highly resistant to heat and to chemicals such as solvents, oxidants, strong acids and bases, *etc.* Since the first report on its preparation by Ishihara in 1986,^[8,9] a variety of single-site group 4 metal based catalysts have been developed, and the most active catalytic systems are titanium precursors formulated as $[\text{LTiX}_3]$, where L is an substituted cyclopentadienyl (Cp), indenyl (Ind), or fluorenyl (Flu) ligand, and X is halogen or alkoxyl moiety.^[1,10,11] However, a certain amount of atactic polystyrene is usually associated with syndiotactic polystyrene due to the different oxidation state of titanium element.

In 2004, rare-earth metal complexes, half-sandwich cati-

onic scandium alkyl species (**I**),^[12] and neutral lanthanidocene (**IX**)^[13,14] were employed to catalyze syndiospecific polymerization of styrene, and a great progress has been made. To date, various rare-earth metal precursors bearing substituted Cp, linked Cp, hetero-Cp, substituted Ind, and Flu ligands have been reported to show distinguished performances for styrene syndiospecific polymerization (**Chart 1**).^[15–25] However, nearly all of them are confined to scandium-based precursors, which is attributed to the intrinsic nature of scandium, electronically close to titanium. The breakthrough was achieved by Cui's group in 2012, in which pyridyl-Cp* ligated lutetium allyl precursor (**X**) displayed very high catalytic activity ($3120 \text{ kg}\cdot\text{mol}_{\text{Ln}}^{-1}\cdot\text{h}^{-1}$) and perfect syndioselectivity (*rrrr* > 99%) for styrene polymerization, but its yttrium analogue still showed much lower activity ($178 \text{ kg}\cdot\text{mol}_{\text{Ln}}^{-1}\cdot\text{h}^{-1}$).^[17] Soon after that, the more powerful ancillary pyridyl-methylene-fluorenyl ligand was developed, with which the scope of rare-earth metal catalysts to exhibit high catalytic activity and high syndioselectivity for styrene polymerization was extended from scandium to praseodymium (**XI**).^[18,19] Moreover, these catalysts demonstrated excellent performance in copolymerization of styrene with other monomers.^[26–35] However, at an attempt of further enhancing the catalytic activity *via* modifying fluorenyl

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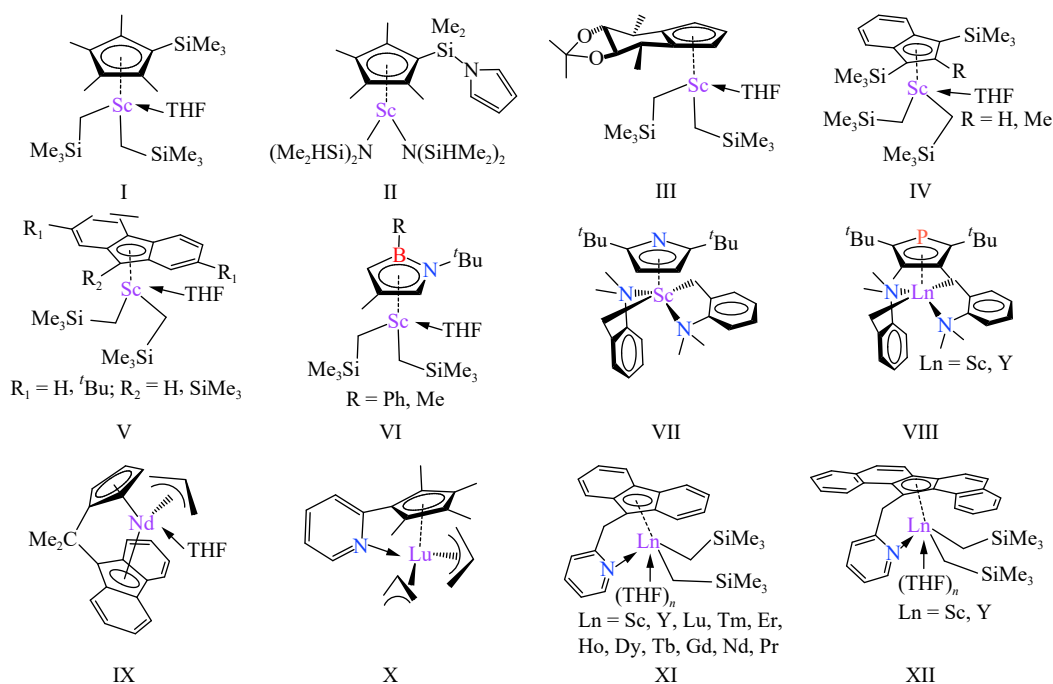


Chart 1 Rare-earth metal based precursors for syndiospecific polymerization of styrene

moiety by electron-withdrawing fragment, sluggish productivity of the yttrium catalyst (XII) was obtained, although the activity of its scandium analogue was increased. These results demonstrated that not only side-arm pyridyl moiety but also fluorenyl fragment played important parts in controlling the polymerization behavior of rare-earth metal catalysts. Therefore, it is necessary to investigate the influence of cyclopentadienyl segment properties on catalyst behavior in order to synthesize more powerful ligand ligated rare-earth metal catalysts for styrene polymerization. In this work, a series of rare-earth metal precursors bearing identical methylene pyridyl side-arm but having various cyclopentadienyl groups ($R = \text{Cp}$ (HL^1), $R = \text{Ind}$ (HL^2), $R = 3\text{-(SiMe}_3\text{)Ind}$ (HL^3), and $R = 2,7\text{-(}^t\text{Bu)Flu}$ (HL^4)) have been synthesized. Polymerization behaviors of these precursors in the styrene homopolymerization were explored.

EXPERIMENTAL

General Considerations

All manipulations were performed under a dry and oxygen-free nitrogen atmosphere using standard high-vacuum Schlenk techniques or in a glovebox. All solvents were purified *via* a SPS system. The monomers were dried over CaH_2 under stirring for 12 h and distilled before use. $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ were purchased from Energy Chemical. Complexes **4a**, **5a**, **5b**, **5c**, and ligands $2,7\text{-}^t\text{Bu}_2\text{C}_{13}\text{H}_7\text{CH}_2\text{Py}$, $\text{C}_5\text{H}_4\text{CH}_2\text{Py}$, $\text{C}_9\text{H}_7\text{CH}_2\text{Py}$ were prepared according to the reported methods.^[18,32]

^1H - and ^{13}C -NMR spectra were recorded on a Bruker AV400 (400 MHz for ^1H -NMR; 100 MHz for ^{13}C -NMR) spectrometer. Elemental analyses were performed using an Elementar Americas Vario MicroCube instrument. The molecular weight and molecular weight distribution of the poly-

mers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220 type high temperature chromatography equipped with three PL-gel 10 μm Mixed-BLS type columns at 150 $^\circ\text{C}$. The glass transition temperature (T_g) of the polymer was measured through differential scanning calorimetry (DSC) analysis, which was carried out on a METTLER TOPEM DSC instrument under nitrogen atmosphere. Any thermal history difference in the polymers was eliminated by first heating the specimen to 300 $^\circ\text{C}$, cooling at 10 $^\circ\text{C}/\text{min}$ to room temperature, and then recording the second DSC scan from 25 $^\circ\text{C}$ to 300 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$.

X-ray Crystallographic Studies

Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at $-86\text{ }^\circ\text{C}$ on a Bruker SMART APEX diffractometer with a CCD area detector and using graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.071\text{ nm}$). The determination of crystal class and unit cell parameters was carried out using the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on F^2 anisotropically for all nonhydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The crystallographic data and structure refinement details of complex **2'** and complex **3a** are summarized in Tables S1 and S2 (in electronic supplementary information, ESI).

Synthesis of $\text{SiMe}_3\text{C}_9\text{H}_6\text{CH}_2\text{Py}$

Under a nitrogen atmosphere, to the THF solution of $\text{C}_9\text{H}_6\text{CH}_2\text{Py}$ (10 mmol, 2.073 g) was slowly added 1 equiv.

of n BuLi (4.00 mL, 2.5 mol/L) at 0 °C. After 3 h, Me_3SiCl (30 mmol, 4.00 mL) was slowly added to the $(\text{C}_9\text{H}_6\text{CH}_2\text{-Py})\text{Li}$ solution at 0 °C. Then the mixture was stirred at room temperature for 12 h to afford a yellow suspension. All volatiles were removed at vacuum and then extracted with n -hexane. The product was purified by distillation at 140 °C in a yield of 77%. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , 25 °C, δ , ppm): -0.05 (s, 9H, SiMe_3), 3.45 (s, 1H, C_9H_6), 4.18 (s, 2H, CH_2), 6.40 (s, 1H, C_9H_6), 7.10 (m, 1H, $\text{C}_5\text{H}_4\text{N}$), 7.15–7.23 (m, 3H, C_9H_6 , $\text{C}_5\text{H}_4\text{N}$), 7.36 (d, 1H, $^3J_{\text{H-H}} = 6.8$ Hz, C_9H_6), 7.43 (d, 1H, $^3J_{\text{H-H}} = 7.2$ Hz), 7.54 (dt, 1H, $^3J_{\text{H-H}} = 8.0$ Hz, $^4J_{\text{H-H}} = 1.6$ Hz, C_{13}H_6), 8.57 (d, 1H, $^3J_{\text{H-H}} = 4.8$ Hz, $\text{C}_5\text{H}_4\text{N}$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , 25 °C, δ , ppm): -2.3 (s, 3C, SiMe_3), 37.4 (s, 1C, CH_2Py), 45.0 (s, 1C, *ipso*- $\text{PyCH}_2\text{C}_9\text{H}_7$), 119.6, 121.2, 122.8, 122.9, 123.8, 124.6, 132.7, 136.3, 139.0, 144.0, 146.2, 149.2 (s, 12C, C_9H_7 , $\text{C}_5\text{H}_4\text{N}$), 160.3 (s, 1C, *ipso*- $\text{C}_5\text{H}_4\text{N}$).

Synthesis of $(\text{C}_5\text{H}_4\text{CH}_2\text{Py})\text{Sc}(\text{CH}_2\text{SiMe}_3)_2$ (1)

In the glovebox, the THF solution of $\text{C}_5\text{H}_4\text{CH}_2\text{Py}$ (1 mmol, 0.157 g) reacted with 1.0 equiv. of n BuLi (0.63 mL, 1.6 mol/L) at room temperature for 30 min. Then, to the THF suspension of ScCl_3 (1.0 mmol, 0.152 g), 1.0 equiv. of $(\text{C}_5\text{H}_4\text{CH}_2\text{Py})\text{Li}$ solution was slowly added at room temperature. The mixture was stirred at room temperature for 12 h to afford a red suspension, to which 2.0 equiv. of $\text{LiCH}_2\text{SiMe}_3$ (2.0 mmol, 0.188 g) was added at -10 °C, and the resulting mixture was stirred overnight to afford a brown solution. Removal of all volatiles, extraction with n -hexane, filtering and recrystallization in hexane solution at -30 °C gave complex **1** as red crystalline solids in a yield of 20%. $^1\text{H-NMR}$ (400 MHz, benzene- d_6 , 25 °C, δ , ppm): 0.08 (s, 4H, CH_2SiMe_3), 0.23 (s, 18H, CH_2SiMe_3), 3.47 (s, 2H, $\text{CH}_2\text{-Py}$), 6.23 (d, 1H, $\text{C}_5\text{H}_4\text{N}$), 6.24 (t, 2H, $^3J_{\text{H-H}} = 5.2$ Hz, Cp), 6.30 (t, 1H, $^3J_{\text{H-H}} = 6.4$ Hz, $\text{C}_5\text{H}_4\text{N}$), 6.59 (t, 2H, $^3J_{\text{H-H}} = 2.8$ Hz, Cp), 6.65 (td, 1H, $^3J_{\text{H-H}} = 8.0$ Hz, $\text{C}_5\text{H}_4\text{N}$), 8.31 (d, 1H, $^3J_{\text{H-H}} = 4.2$ Hz, $\text{C}_5\text{H}_4\text{N}$).

Synthesis of $(\text{C}_9\text{H}_6\text{CH}_2\text{Py})_2\text{Sc}(\text{CH}_2\text{SiMe}_3)_2$ (2')

In the glovebox, 1.0 equiv. of $\text{C}_9\text{H}_6\text{CH}_2\text{Py}$ (0.103 g, 0.5 mmol) in THF (2 mL) was slowly added into the THF solution of $\text{Sc}(\text{CH}_2\text{SiMe}_3)_3\text{THF}_2$ (0.225 g, 0.5 mmol) at ambient temperature. Then the mixture was stirred at ambient temperature for 30 min. All volatiles were removed at vacuum and the crystalline product was isolated from the hexane/toluene solution in a yield of 40%. $^1\text{H-NMR}$ (400 MHz, C_6D_6 , 25 °C, δ , ppm): -1.90 (s, 0.5H, $\text{ScCH}_2\text{SiMe}_3$), -1.58 (s, 0.5H, $\text{ScCH}_2\text{SiMe}_3$), -0.35 (s, 1H, $\text{ScCH}_2\text{SiMe}_3$), 0.05 (s, 9H, $\text{ScCH}_2\text{SiMe}_3$), 2.67 (s, 1H, CH_2 in bridge), 2.98 (s, 2H, CH_2 in bridge), 3.17 (s, 1H, CH_2 in bridge), 4.0 (m, 4H, C_9H_7), 5.12 (d, 1H, C_9H_7), 5.76 (s, 1H, C_9H_7), 6.25 (m, 2H, C_9H_7), 6.48 (s, 1H, C_9H_7), 6.87 (m, 8H, $\text{C}_5\text{H}_4\text{N}$, C_9H_7), 7.67 (m, 3H, $\text{C}_5\text{H}_4\text{N}$), 8.29 (d, $^3J_{\text{H-H}} = 4.8$ Hz, 2H, $\text{C}_5\text{H}_4\text{N}$). Anal. Calcd. for $\text{C}_{32}\text{H}_{35}\text{N}_2\text{ScSi}$ (%): C, 73.82, H, 6.77, N, 5.38. Found: C, 73.93, H, 6.79, N, 5.31.

Synthesis of $(\text{C}_9\text{H}_6\text{CH}_2\text{Py})\text{Sc}(\text{CH}_2\text{SiMe}_3)_2$ (2)

In the glove box, the THF solution of $\text{C}_9\text{H}_7\text{CH}_2\text{Py}$ (1 mmol, 0.207 g) reacted with 1.0 equiv. of n BuLi (0.63 mL, 1.6 mol/L) at room temperature for 30 min. Then, to the THF

suspension of ScCl_3 (1.0 mmol, 0.152 g), 1.0 equiv. of a $(\text{C}_9\text{H}_6\text{CH}_2\text{Py})\text{Li}$ solution was added slowly at room temperature. The mixture was stirred at room temperature for 12 h to afford a yellow suspension, to which 2.0 equiv. of $\text{LiCH}_2\text{SiMe}_3$ (2.0 mmol, 0.188 g) was added at -10 °C, and the resulting mixture was stirred overnight to afford a brown solution. Removal of all volatile compounds, extraction with n -hexane, and recrystallization in hexane solution at -30 °C gave complex **2** as a yellow crystalline solid in a yield of 71%. $^1\text{H-NMR}$ (400 MHz, benzene- d_6 , 25 °C, δ , ppm): -1.24 , -1.21 (AB, $^2J_{\text{H-H}} = 9.6$ Hz, 1H, CH_2SiMe_3), -0.83 , -0.80 (AB, $^2J_{\text{H-H}} = 11.2$ Hz, 1H, CH_2SiMe_3), 0.04, 0.07 (AB, $^2J_{\text{H-H}} = 10.4$ Hz, 1H, CH_2SiMe_3), 0.30, 0.27 (AB, $^3J_{\text{H-H}} = 10.4$ Hz, 1H, CH_2SiMe_3), 0.16 (s, 9H, CH_2SiMe_3), 0.21 (s, 9H, CH_2SiMe_3), 3.73, 3.78 (AB, 1H, $^2J_{\text{H-H}} = 18.8$ Hz, CH_2Py), 3.90, 3.95 (AB, 1H, $^2J_{\text{H-H}} = 18.8$ Hz, CH_2Py), 6.29 (t, 1H, $^3J_{\text{H-H}} = 6.8$ Hz, $\text{C}_5\text{H}_4\text{N}$), 6.45 (d, 1H, $^3J_{\text{H-H}} = 10.0$ Hz, $\text{C}_5\text{H}_4\text{N}$), 6.66 (d, 1H), 6.73 (t, 1H, $^3J_{\text{H-H}} = 7.6$ Hz, $\text{C}_5\text{H}_4\text{N}$), 6.85 (d, 1H, $^3J_{\text{H-H}} = 3.2$ Hz, C_9H_7), 6.94–7.01 (m, 2H, C_9H_7), 7.82 (d, 1H, $^3J_{\text{H-H}} = 8.2$ Hz, C_9H_6), 8.33 (d, 1H, $^3J_{\text{H-H}} = 5.2$ Hz, $\text{C}_5\text{H}_4\text{N}$). $^{13}\text{C-NMR}$ (100 MHz, benzene- d_6 , 25 °C, δ , ppm): 3.8 (s, 6C, CH_2SiMe_3), 34.1 (s, 1C, CH_2Py), 40.3 (s, 1C, CH_2SiMe_3), 46.7 (s, 1C, CH_2SiMe_3), 99.6 (s, 1C, *ipso*- C_9H_6), 110.3 (s, 1C, C_9H_6), 120.4 (s, 1C, C_9H_6), 121.9 (s, 1C, C_9H_6), 122.0 (s, 1C, C_9H_6), 122.6 (s, 1C, C_9H_6), 123.7 (s, 1C, $\text{C}_5\text{H}_4\text{N}$), 125.4 (s, 1C, $\text{C}_5\text{H}_4\text{N}$), 127.2 (s, 1C, C_9H_6), 129.2 (s, 1C, C_9H_6), 139.2 (s, 1C, $\text{C}_5\text{H}_4\text{N}$), 147.7 (s, 1C, $\text{C}_5\text{H}_4\text{N}$), 170.0 (s, 1C, *ipso*- $\text{C}_5\text{H}_4\text{N}$). Anal. Calcd. for $\text{C}_{23}\text{H}_{36}\text{NScSi}_2$ (%): C, 64.59; H, 8.48; N, 3.28. Found: C, 64.64; H, 8.41; N, 3.25.

Synthesis of $(\text{SiMe}_3\text{C}_9\text{H}_5\text{CH}_2\text{Py})\text{Sc}(\text{CH}_2\text{SiMe}_3)_2$ (3a)

In the glove box, the THF solution of $\text{SiMe}_3\text{C}_9\text{H}_5\text{CH}_2\text{Py}$ (1 mmol, 0.278 g) reacted with 1.0 equiv. of n BuLi (0.63 mL, 1.6 mol/L) at room temperature for 30 min. Then, to the THF suspension of ScCl_3 (1.0 mmol, 0.152 g), 1.0 equiv. of a $(\text{SiMe}_3\text{C}_9\text{H}_5\text{CH}_2\text{Py})\text{Li}$ solution was added slowly at room temperature. The mixture was stirred at room temperature for 12 h to afford a yellow suspension, to which 2.0 equiv. of $\text{LiCH}_2\text{SiMe}_3$ (2.0 mmol, 0.188 g) was added at -10 °C, and the resulting mixture was stirred overnight to afford a brown solution. Removal of all volatile compounds, extraction with n -hexane, and recrystallization in hexane solution at -30 °C gave complex **3a** as a yellow crystalline solid in a yield of 66%. $^1\text{H-NMR}$ (400 MHz, benzene- d_6 , 25 °C, δ , ppm): -1.10 , -1.07 (AB, $^2J_{\text{H-H}} = 11.6$ Hz, 1H, CH_2SiMe_3), -1.02 , -0.99 (AB, $^2J_{\text{H-H}} = 11.6$ Hz, 1H, CH_2SiMe_3), -0.02 (s, 9H, Ind-SiMe_3), 0.14, 0.17 (AB, $^2J_{\text{H-H}} = 11.2$ Hz, 1H, CH_2SiMe_3), 0.23 (s, 9H, CH_2SiMe_3), 0.43, 0.46 (AB, $^2J_{\text{H-H}} = 11.2$ Hz, 1H, CH_2SiMe_3), 0.62 (s, 9H, CH_2SiMe_3), 3.92 (s, 2H, CH_2Py), 6.33 (t, 1H, $^3J_{\text{H-H}} = 6.4$ Hz, $\text{C}_5\text{H}_4\text{N}$), 6.49 (d, 1H, $^3J_{\text{H-H}} = 8.0$ Hz, $\text{C}_5\text{H}_4\text{N}$), 6.74 (td, 1H, $^3J_{\text{H-H}} = 8.0$ Hz, $^4J_{\text{H-H}} = 1.6$ Hz, $\text{C}_5\text{H}_4\text{N}$), 6.92–6.99 (m, 2H, C_9H_5), 7.14 (s, 1H, C_9H_5), 7.17–7.20 (m, 1H, C_9H_5), 8.00 (dt, 1H, $^3J_{\text{H-H}} = 8.8$ Hz, $^4J_{\text{H-H}} = 1.2$ Hz, C_{13}H_6), 8.47 (d, 1H, $^3J_{\text{H-H}} = 5.6$ Hz, $\text{C}_5\text{H}_4\text{N}$). $^{13}\text{C-NMR}$ (100 MHz, benzene- d_6 , 25 °C, δ , ppm): 0.65 (s, 3C, Ind-SiMe_3), 3.84 (s, 3C, CH_2SiMe_3), 4.01 (s, 3C, CH_2SiMe_3), 34.1 (s, 1C, CH_2Py), 40.0 (s, 1C, CH_2SiMe_3), 46.7 (s, 1C, CH_2SiMe_3), 108.7 (s, 1C, *ipso*- C_9H_5), 114.1 (s,

1C, Me₃Si-C₉H₅), 120.9 (s, 1C, C₉H₅), 122.0 (s, 1C, C₉H₅), 123.0 (s, 2C, C₉H₅), 123.7 (s, 1C, C₉H₅), 126.7 (s, 1C, C₅H₄N), 129.5 (s, 1C, C₅H₄N), 129.9 (s, 1C, C₉H₅), 135.0 (s, 1C, C₉H₅), 139.5 (s, 1C, C₅H₄N), 147.9 (s, 1C, C₅H₄N), 169.6 (s, 1C, *ipso*-C₅H₄N). Anal. Calcd. for C₂₆H₄₄NSeSi₃ (%): C, 62.48; H, 8.87; N, 2.80. Found: C, 62.68; H, 8.90; N, 2.79.

Synthesis of (SiMe₃C₉H₅CH₂Py)Lu(CH₂SiMe₃)₂ (**3b**)

In the glove box, the THF solution of SiMe₃C₉H₆CH₂Py (1 mmol, 0.278 g) reacted with 1.0 equiv. of ⁿBuLi (0.63 mL, 1.6 mol/L) at room temperature for 30 min. Then, to the THF suspension of LuCl₃ (1.0 mmol, 0.281 g), 1.0 equiv. of a (SiMe₃C₉H₆CH₂Py)Li solution was added slowly at room temperature. The mixture was stirred at room temperature for 12 h to afford a yellow suspension, to which 2.0 equiv. of LiCH₂SiMe₃ (2.0 mmol, 0.188 g) was added at -10 °C, and the resulting mixture was stirred overnight to afford a brown solution. Removal of all volatile compounds, extraction with *n*-hexane, and recrystallization in hexane solution at -30 °C gave complex **3b** as a yellow crystalline solid in a yield of 75%. ¹H-NMR (400 MHz, benzene-d₆, 25 °C, δ, ppm): -1.69 (br, 1H, CH₂SiMe₃), -1.48 (br, 1H, CH₂SiMe₃), -0.65 (br, 1H, CH₂SiMe₃), -0.34 (br, 1H, CH₂SiMe₃), 0.15 (s, 18H, CH₂SiMe₃), 0.58 (s, 9H, Ind-SiMe₃), 1.41 (4H, THF), 3.59 (4H, THF), 3.90, 3.95 (AB, 1H, ²J_{H-H} = 18.8 Hz, CH₂Py), 3.96, 4.01 (AB, 1H, ²J_{H-H} = 18.4 Hz, CH₂Py), 6.34 (t, 1H, ³J_{H-H} = 6.4 Hz, C₅H₄N), 6.50 (d, 1H, ³J_{H-H} = 8.0 Hz, C₅H₄N), 6.99 (m, 3H, C₉H₅, C₅H₄N), 7.15–7.19 (m, 3H, C₉H₅), 7.95 (dt, 1H, ³J_{H-H} = 8.4 Hz, ⁴J_{H-H} = 1.6 Hz, C₉H₅), 8.29 (d, 1H, ³J_{H-H} = 5.2 Hz, C₅H₄N). ¹³C-NMR (100 MHz, benzene-d₆, 25 °C, δ, ppm): 0.84 (s, 3C, Ind-SiMe₃), 4.56 (s, 6C, CH₂SiMe₃), 25.6 (2C, THF), 34.2 (s, 1C, CH₂Py), 39.4 (s, 2C, CH₂SiMe₃), 42.9 (s, 2C, CH₂SiMe₃), 67.0 (2C, THF), 105.2 (s, 1C, *ipso*-C₉H₅), 111.8 (s, 1C, Me₃Si-C₉H₆), 120.5 (s, 1C, C₉H₆), 121.9 (s, 1C, C₉H₅), 122.2 (s, 1C, C₉H₅), 122.3 (s, 1C, C₉H₅), 124.1 (s, 1C, C₉H₅), 125.4 (s, 1C, C₅H₄N), 128.4 (s, 1C, C₅H₄N), 129.2 (s, 1C, C₉H₅), 134.5 (s, 1C, C₉H₅), 139.1 (s, 1C, C₅H₄N), 147.8 (s, 1C, C₅H₄N), 169.5 (s, 1C, *ipso*-C₅H₄N). Anal. Calcd. for C₃₀H₅₂NLuSi₃ (%): C, 51.33; H, 7.47; N, 2.00. Found: C, 51.53; H, 7.49; N, 1.92.

Synthesis of (SiMe₃C₉H₅CH₂Py)Y(CH₂SiMe₃)₂ (**3c**)

In the glove box, the THF solution of SiMe₃C₉H₆CH₂Py (1 mmol, 0.278 g) reacted with 1.0 equiv. of ⁿBuLi (0.63 mL, 1.6 mol/L) at room temperature for 30 min. Then, to the THF suspension of YCl₃ (1.0 mmol, 0.195 g), 1.0 equiv. of a (SiMe₃C₉H₆CH₂Py)Li solution was added slowly at room temperature. The mixture was stirred at room temperature for 12 h to afford a yellow suspension, to which 2.0 equiv. of LiCH₂SiMe₃ (2.0 mmol, 0.188 g) was added at -10 °C, and the resulting mixture was stirred overnight to afford a brown solution. Removal of all volatile compounds, extraction with *n*-hexane, and recrystallization in hexane solution at -30 °C gave complex **3c** as a yellow crystalline solid in a yield of 74%. ¹H-NMR (400 MHz, benzene-d₆, 25 °C, δ, ppm): -1.64 (br, 1H, CH₂SiMe₃), -1.32 (br, 1H, CH₂SiMe₃), -0.66 (br, 1H, CH₂SiMe₃), -0.52 (br, 1H, CH₂SiMe₃), 0.12 (s, 18H, CH₂SiMe₃), 0.50 (s, 9H, Ind-SiMe₃), 1.37 (4H, THF), 3.64

(4H, THF), 4.04, 4.08 (AB, 1H, ²J_{H-H} = 18.8 Hz, CH₂Py), 4.15, 4.20 (AB, 1H, ²J_{H-H} = 18.8 Hz, CH₂Py), 6.52 (t, 1H, ³J_{H-H} = 6.4 Hz, C₅H₄N), 6.61 (d, 1H, ³J_{H-H} = 8.0 Hz, C₅H₄N), 6.84 (td, 1H, ³J_{H-H} = 7.6 Hz, ⁴J_{H-H} = 1.6 Hz, C₅H₄N), 7.03–7.08 (m, 3H, C₉H₅), 7.25–7.29 (m, 1H, C₉H₅), 7.75–7.78 (m, 1H, C₉H₆), 8.64 (d, 1H, ³J_{H-H} = 5.2 Hz, C₅H₄N). ¹³C-NMR (100 MHz, benzene-d₆, 25 °C, δ, ppm): 1.32 (s, 3C, Ind-SiMe₃), 4.70 (s, 6C, CH₂SiMe₃), 25.4 (2C, THF), 34.6 (s, 1C, CH₂Py), 31.3 (s, 1C, CH₂SiMe₃), 35.2 (s, 1C, CH₂SiMe₃), 70.3 (2C, THF), 105.2 (s, 1C, *ipso*-C₉H₅), 113.5 (s, 1C, Me₃Si-C₉H₅), 120.9 (s, 1C, C₉H₅), 121.4 (s, 2C, C₉H₅), 121.5 (s, 1C, C₉H₅), 123.5 (s, 1C, C₉H₅), 123.9 (s, 1C, C₉H₅), 126.7 (s, 1C, C₅H₄N), 128.3 (s, 1C, C₅H₄N), 130.1 (s, 1C, C₉H₆), 134.2 (s, 1C, C₉H₅), 138.1 (s, 1C, C₅H₄N), 150.0 (s, 1C, C₅H₄N), 167.9 (s, 1C, *ipso*-C₅H₄N). Anal. Calcd. for C₃₀H₅₂NYSi₃ (%): C, 58.50; H, 8.51; N, 2.27. Found: C, 58.73; H, 8.92; N, 2.77.

Synthesis of (2,7-^tBu₂C₁₃H₆CH₂Py)Lu(CH₂SiMe₃)₂ (**4b**)

In the glove box, the THF solution of 2,7-^tBu₂C₁₃H₇CH₂Py (1 mmol, 0.369 g) reacted with 1.0 equiv. of ⁿBuLi (0.63 mL, 1.6 mol/L) at room temperature for 30 min. Then, to the THF suspension of LuCl₃ (1.0 mmol, 0.281 g), 1.0 equiv. of a 2,7-^tBu₂C₁₃H₆CH₂PyLi solution was added slowly at room temperature. The mixture was stirred at room temperature for 12 h to afford a yellow suspension, to which 2.0 equiv. of LiCH₂SiMe₃ (2.0 mmol, 0.188 g) was added at -10 °C, and the resulting mixture was stirred overnight to afford a brown solution. Removal of all volatile compounds, extraction with *n*-hexane, and recrystallization in hexane solution at -30 °C gave complex **4b** as a yellow crystalline solid in a yield of 82%. ¹H-NMR (400 MHz, benzene-d₆, 25 °C, δ, ppm): -1.80 (br, 2H, CH₂SiMe₃), -1.39 (br, 2H, CH₂SiMe₃), 0.08 (s, 18H, CH₂SiMe₃), 1.38 (t, 2H, THF), 1.44 (s, 18H, CMe₃), 3.47 (t, 2H, THF), 4.54 (s, 2H, CH₂Py), 6.62 (t, 1H, ³J_{H-H} = 6.0 Hz, C₅H₄N), 6.85 (d, 1H, ³J_{H-H} = 8.0 Hz, C₅H₄N), 6.96 (t, 1H, ³J_{H-H} = 8.0 Hz, ⁴J_{H-H} = 1.2 Hz, C₅H₄N), 7.25 (dd, 2H, ³J_{H-H} = 8.0 Hz, ⁴J_{H-H} = 1.6 Hz, C₁₃H₆), 7.39 (m, 2H, C₁₃H₆), 7.97 (d, 2H, ³J_{H-H} = 8.4 Hz, C₁₃H₆), 8.76 (d, 1H, ³J_{H-H} = 5.6 Hz, C₅H₄N). ¹³C-NMR (100 MHz, C₆D₆, 25 °C, δ, ppm): 4.57 (s, 6C, CH₂SiMe₃), 25.4 (s, 2C, THF), 31.8 (s, 6C, CMe₃), 33.0 (s, 1C, CH₂Py), 35.2 (s, 2C, CMe₃), 39.1 (s, 2C, CH₂SiMe₃), 70.9 (s, 2C, THF), 90.0 (s, 1C, *ipso*-C₁₃H₆), 114.5 (s, 2C, C₁₃H₆), 117.0 (s, 2C, C₁₃H₆), 117.9 (s, 2C, C₁₃H₆), 121.3 (s, 1C, C₅H₄N), 121.5 (s, 2C, C₁₃H₆), 124.1 (s, 1C, C₅H₄N), 132.3 (s, 2C, C₁₃H₆), 138.4 (s, 1C, C₅H₄N), 146.8 (s, 1C, C₅H₄N), 149.9 (s, 2C, C₁₃H₆), 166.7 (s, 1C, *ipso*-C₅H₄N). Anal. Calcd. for C₃₉H₆₀LuNOSi₂ (%): C, 59.29; H, 7.66; N, 1.77. Found: C, 59.15; H, 7.62; N, 1.74.

Synthesis of (2,7-^tBu₂C₁₃H₆CH₂Py)Y(CH₂SiMe₃)₂ (**4c**)

In the glove box, the THF solution of 2,7-^tBu₂C₁₃H₇CH₂Py (1 mmol, 0.369 g) reacted with 1.0 equiv. of ⁿBuLi (0.63 mL, 1.6 mol/L) at room temperature for 30 min. Then, to the THF suspension of YCl₃ (1.0 mmol, 0.195 g), 1.0 equiv. of a 2,7-^tBu₂C₁₃H₆CH₂PyLi solution was added slowly at room temperature. The mixture was stirred at room temperature for 12 h to afford a yellow suspension, to which 2.0 equiv. of LiCH₂SiMe₃ (2.0 mmol, 0.188 g) was added at -10 °C, and

the resulting mixture was stirred overnight to afford a brown solution. Removal of all volatile compounds, extraction with *n*-hexane, and recrystallization in hexane solution at $-30\text{ }^{\circ}\text{C}$ gave complex **4c** as a yellow crystalline solid in a yield of 79%. $^1\text{H-NMR}$ (400 MHz, benzene- d_6 , $25\text{ }^{\circ}\text{C}$, δ , ppm): -1.48 (br, 4H, CH_2SiMe_3), 0.08 (s, 18H, CH_2SiMe_3), 1.40 (t, 2H, THF), 1.44 (s, 18H, CMe_3), 3.54 (t, 2H, THF), 4.58 (s, 2H, CH_2Py), 6.66 (t, 1H, $^3J_{\text{H-H}} = 6.4\text{ Hz}$, $\text{C}_5\text{H}_4\text{N}$), 6.89 (d, 1H, $^3J_{\text{H-H}} = 8.0\text{ Hz}$, $\text{C}_5\text{H}_4\text{N}$), 6.99 (td, 1H, $^3J_{\text{H-H}} = 7.6\text{ Hz}$, $^4J_{\text{H-H}} = 1.6\text{ Hz}$, $\text{C}_5\text{H}_4\text{N}$), 7.23 (dd, 2H, $^3J_{\text{H-H}} = 8.8\text{ Hz}$, $^4J_{\text{H-H}} = 1.6\text{ Hz}$, $\text{C}_5\text{H}_4\text{N}$), 7.27 (s, 1H, C_{13}H_6), 7.93 (d, 2H, $^3J_{\text{H-H}} = 8.4\text{ Hz}$, C_{13}H_6), 8.85 (d, 1H, $^3J_{\text{H-H}} = 5.2\text{ Hz}$, $\text{C}_5\text{H}_4\text{N}$). $^{13}\text{C-NMR}$ (100 MHz, C_6D_6 , $25\text{ }^{\circ}\text{C}$, δ , ppm): 4.5 (s, 6C, CH_2SiMe_3), 25.4 (s, 2C, THF), 31.8 (s, 6C, CMe_3), 33.2 (s, 1C, CH_2Py), 35.3 (s, 2C, CMe_3), 34.6 (d, $J_{\text{Y-C}} = 40\text{ Hz}$, 1C, CH_2SiMe_3), 70.7 (s, 2C, THF), 92.2 (s, 1C, *ipso*- C_{13}H_6), 114.5 (s, 2C, C_{13}H_6), 116.8 (s, 2C, C_{13}H_6), 117.1 (s, 2C, C_{13}H_6), 121.3 (s, 1C, $\text{C}_5\text{H}_4\text{N}$), 121.5 (s, 2C, C_{13}H_6), 123.9 (s, 1C, $\text{C}_5\text{H}_4\text{N}$), 131.9 (s, 2C, C_{13}H_6), 138.3 (s, 1C, $\text{C}_5\text{H}_4\text{N}$), 146.9 (s, 1C, $\text{C}_5\text{H}_4\text{N}$), 150.4 (s, 2C, C_{13}H_6), 167.1 (s, 1C, *ipso*- $\text{C}_5\text{H}_4\text{N}$). Anal. Calcd. for $\text{C}_{39}\text{H}_{60}\text{YNOSi}_2$ (%): C, 66.54; H, 8.59; N, 1.99; Found: C, 66.23; H, 8.62; N, 1.89.

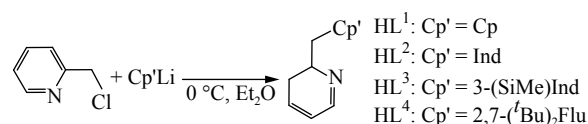
Typical Procedure for Styrene Polymerization

In a glovebox, 1.04 g (10 mmol) of styrene was added to a toluene solution (0.2 mL) of Al^iBu_3 (0.5 mol/L) in a 10 mL flask. Then, a toluene solution (0.8 mL) of **4a** (5.9 mg, 10 μmol) and 1.0 equiv. of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (9.2 mg, 10 μmol) was added to the flask. After the mixture was stirred for 1 min, the ethanol solution with BHT was injected to terminate the polymerization. The mixture was poured into a large amount of ethanol to precipitate the polymer product. The obtained white solid product was filtered and then dried under vacuum at $45\text{ }^{\circ}\text{C}$ to a constant weight.

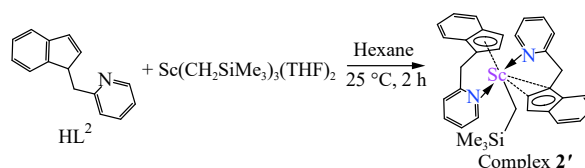
RESULTS AND DISCUSSION

Preparation of CGC Rare-earth Metal Dialkyl Complexes 1–4

The pyridyl-methylene-functionalized Cp, Ind, and Flu compounds HL^{1-4} were synthesized in moderate to high yields (47%–63%) by salt metathesis reaction of chloromethylpyridine with the corresponding cyclopentadienyl lithium salts (Scheme 1). In general, rare-earth metal dialkyl complexes could be prepared by deprotonating neutral ligand by rare-earth metal tris(alkyl)s with releasing SiMe_4 .^[3,36,37] Unexpectedly, the attempt to prepare scandium dialkyl complex **1** via alkyl elimination of scandium tris(alkyl)s with HL^1 failed with the formation of undefined products. Treatment of HL^2 with $\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ at room temperature for 1 h afforded a mono(alkyl) scandium complex **2'** [$(\text{Cp-CH}_2\text{-Py})_2\text{ScCH}_2\text{SiMe}_3$] in 40% yield (Scheme 2), which was confirmed by $^1\text{H-NMR}$ spectroscopy and X-ray diffraction analysis (Fig. 1). Even for the steric demanding pyridyl-methylene-fluorene, the desired bis(alkyl) complex **5** was obtained in a much lower yield by means of alkyl abstraction pathway.^[18,19] These results demonstrated that alkyl abstraction is not a feasible method to prepare pyridyl-methylene-attached Cp derivatives.



Scheme 1 Syntheses of Cp/Ind/Flu- CH_2Py ligands HL^{1-4}



Scheme 2 Synthesis of Complex **2'**

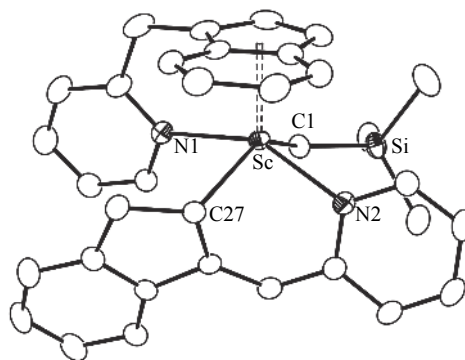
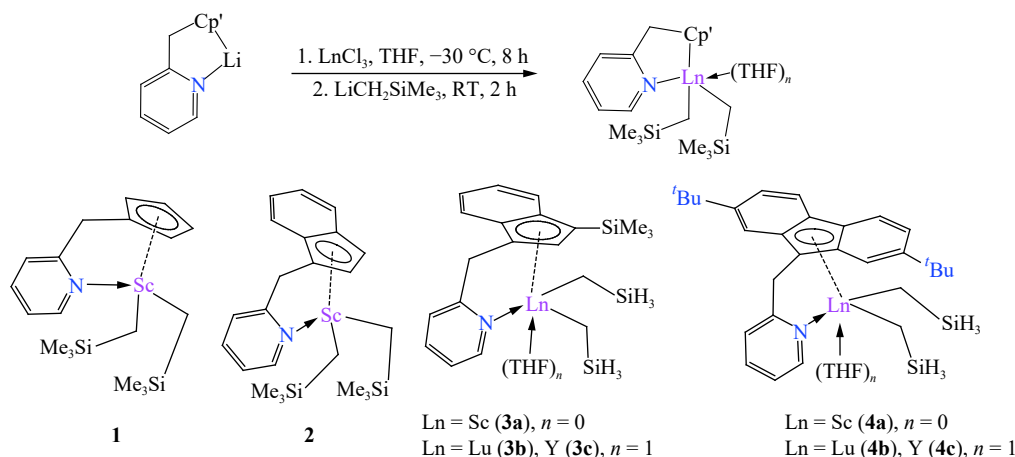


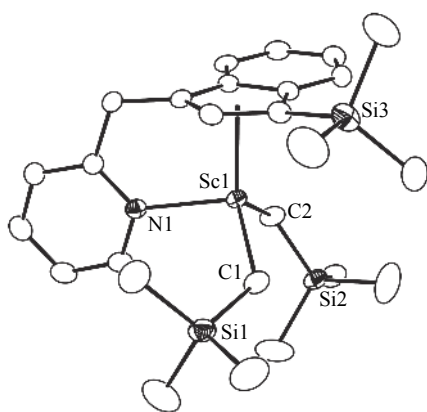
Fig. 1 X-ray structure of **2'** with 40% probability of thermal ellipsoids.

Hence, we tried to prepare target rare-earth metal bis(alkyl) complexes by sequential metathesis reaction between alkaline ligand salts and rare-earth metal trichlorides followed by reaction with alkyl lithium reagents (Scheme 3). In the end, the pyridyl-methylene-cyclopentadienyl-stabilized dialkyl complexes were produced in moderate to good yields (20%–72%), which were confirmed by $^1\text{H-NMR}$ spectroscopic analyses. The methylene protons of $\text{LnCH}_2\text{SiMe}_3$ species and $\text{Py-CH}_2\text{-Cp}$ moiety of complex **1** appeared at $\delta = 0.08$ and 3.47 ppm and no proton resonances from THF were observed, indicating a THF-free complex. The methylene bridge between indenyl and pyridyl moieties of complex **2** gave AB spins at $\delta = 3.76$ and 3.93 ppm , stemming from asymmetric configuration space. For the same reason, the methylene protons of $\text{ScCH}_2\text{SiMe}_3$ species were diastereotopic, giving two independent AB spins at $\delta = -1.23/-0.82$ and $0.06/0.29\text{ ppm}$.^[38] The methylene protons in complex **3a** only exhibited a sharp single peak at $\delta = 3.92\text{ ppm}$, but the methylene protons of $\text{ScCH}_2\text{SiMe}_3$ species still gave AB spins at $\delta = -1.08/-1.01$ and $0.16/0.45\text{ ppm}$. The diastereotopic structure of complex **3a** was also confirmed by X-ray diffraction analysis, as monomeric bis(alkyl) complex without ligated THF solvent (Fig. 2). The structures of its lutetium and yttrium analogues **3b** and **3c** were certificated as monomeric bis(alkyl) complexes bearing one THF molecule by NMR spectroscopic analyses.

Previously, we have demonstrated that the $\text{Py-CH}_2\text{-2,7-(}^t\text{Bu)}_2\text{-Flu}$ stabilized complex **4a** is a THF-free bis(alkyl) complex that showed extremely high catalytic activity for 4-



Scheme 3 Syntheses of rare-earth metal bis(alkyl) complexes 1–4

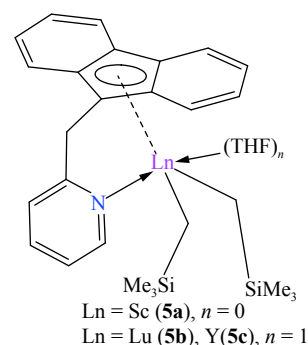
Fig. 2 X-ray structure of **3a** with 35% probability of thermal ellipsoids.

isopropenestyrene polymerization.^[32] In this work, its lutetium and yttrium analogues **4b** and **4c** were prepared *via* one-pot metathesis reaction between HL⁴ lithium salt, rare-earth metal chlorides, and alkyl lithium. ¹H-NMR spectroscopic analyses of complexes **4b** and **4c** showed that Flu-H protons of the ligands disappeared while the methylene protons of Ln-CH₂SiMe₃ appeared at $\delta = -1.80/-1.39$ and $\delta = -1.48$ ppm, respectively. Both methylene spacers between fluorenyl and pyridyl groups gave sharp single peaks at $\delta = 4.54$ ppm in complex **4b** and $\delta = 4.58$ ppm in complex **4c** due to their symmetric coordination environments. ¹H-NMR and ¹³C-NMR spectroscopic analyses demonstrated that both complexes **4b** and **4c** were solvated by one THF molecular. All these complexes were readily soluble in hexane, toluene, THF or diethyl ether, *etc.*

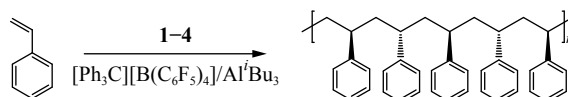
Styrene Polymerization

All complexes were inert in styrene polymerization separately. It is unexpected that activated by 1.0 equiv. of [Ph₃C][B(C₆F₅)₄], complex **1** also showed very low activity towards styrene polymerization, even in the presence of 10 equiv. of Al^{*i*}Bu₃, suggesting that both the cyclopentadienyl segment and the side-arm pyridyl moiety play important roles in controlling the catalyst's activity. According to the literatures reported,^[19,25] enhancing electron-withdrawing

ability of cyclopentadienyl group is beneficial to improving catalyst's activity. Thereby, complex **2** containing indenyl moiety was synthesized and used to initiate styrene polymerization in combination with [Ph₃C][B(C₆F₅)₄] and Al^{*i*}Bu₃. However, its catalytic activity for styrene polymerization was still very low as that of complex **1**. Hou and Chen reported that electron-withdrawing SiMe₃ modified tetramethylcyclopentadienyl or indenyl ligand displayed very high activity for styrene polymerization.^[12,25] Therefore, the trimethylsilyl modified pyridyl-methylene-indenyl complex **3a** was synthesized. As expected, its catalytic activity was really improved, but still much lower than that of complex **5** (Fig. 3). Furthermore, when their lutetium and yttrium analogues were employed, the polymerization became very sluggish.

Fig. 3 Structure of complexes **5a–5c**

In our previous work, modifying the fluorenyl segment by introducing phenyl rings could effectively boost the catalytic activity of its scandium complex, but deteriorated those of its lutetium and yttrium analogues.^[19] To further explore the substituent effect of cyclopentadienyl segment on polymerization activity, *tert*-butyl moieties were introduced into 2,7-positions of fluorenyl segment of complex **5**. Unexpectedly, complex **4a** modified with electron-donating ^{*t*}Bu group exhibited extremely high catalytic activity for styrene polymerization, which could convert 5000 equiv. of styrene within 10 min to afford polystyrene with a high molecular weight (24.0×10^4) and a moderate molecular weight distribution

Table 1 Homopolymerization of St by using **1–4** precursors ^a

Run	Cat.	[M]/[Ln] (mol/mol)	Time (min)	Conv. (%)	<i>rrrr</i> ^b (%)	$M_n^c \times 10^{-4}$	M_w/M_n^c	T_g^d (°C)	T_m^d (°C)
1	1a	1000	180	5	n.d.	0.6	2.29	96	260
2	2a	1000	180	6	n.d.	1.4	3.07	97	260
3	3a	1000	20	46	> 99	3.5	2.09	95	269
4	3b	1000	180	5	n.d.	0.7	2.21	83	243
5	3c	1000	180	5	n.d.	0.9	1.62	95	258
6	4a	1000	1	100	> 99	7.2	2.46	99	271
7	4a	3000	5	100	> 99	15.4	2.41	99	270
8	4a	5000	10	100	> 99	24.0	2.49	99	270
9	4b	1000	1	100	> 99	12.2	1.56	99	270
10	4b	3000	10	100	> 99	32.9	1.94	100	270
11	4b	5000	15	90	> 99	48.7	1.91	100	270
12	4c	1000	1	100	> 99	18.2	1.28	100	270
13	4c	2000	4	100	> 99	28.8	1.67	100	271
14	4c	3000	6	100	> 99	36.7	1.68	100	271
15	4c	4000	10	100	> 99	47.2	1.75	100	270
16	4c	5000	15	97	> 99	54.1	1.85	100	271

^a Polymerization conditions: catalyst [Ln] (10 μmol), [Ln]/[Ph₃C][B(C₆F₅)₄]/AlⁱBu₃ = 1/1/10 (mol/mol/mol), [St] = 1.7 mol/L in toluene, T_p = 25 °C, unless otherwise noted; ^b Measured by ¹³C-NMR spectroscopy in C₆D₂Cl₂ at 100 °C; ^c Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against a polystyrene standard; ^d Determined by DSC

(PDI = 2.49) (Table 1, run 8). Excitedly, the introduction of *tert*-butyl groups at 2 and 7 positions of fluorenyl segment did not deactivate its lutetium and yttrium analogues, which is in sharp contrast to those of pyridyl-methylene-dibenzo-[*a,i*]fluorenyl stabilized rare-earth metal complexes.^[19] In order to differentiate the effect of ^tBu group on catalyst's activity, styrene homopolymerizations were carried out in a diluted toluene solution (0.32 mol/L). Through controlled trials, we found that ^tBu-modified complexes **4a**, **4b**, and **4c** showed much higher catalytic activities than their analogues **5a**, **5b**, and **5c** (Table 2).

Table 2 Homopolymerization of St by using **4a–4c** and **5a–5c** precursors ^a

Run	Cat.	[M]/[Ln] (mol/mol)	Time (min)	Conv. (%)	$M_n^b \times 10^{-4}$	M_w/M_n^b
1	4a	500	25s	97	7.4	1.78
2	5a	500	25s	26	3.6	1.98
3	4b	500	2	50	6.7	1.56
4	5b	500	2	12	4.0	1.80
5	4c	500	2	56	4.9	1.26
6	5c	500	2	34	3.8	1.28

^a Polymerization conditions: [Ln] (10 μmol), [Ln]/[Ph₃C][B(C₆F₅)₄]/AlⁱBu₃ = 1/1/10 (mol/mol/mol), [St] = 0.32 mol/L in toluene, T_p = 25 °C, unless otherwise noted; ^b Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against a polystyrene standard

Due to their low yield in styrene polymerization, the obtained polystyrenes generated by complexes **1**, **2**, **4**, and **5** are not enough to conduct ¹H- and ¹³C-NMR spectroscopic analysis. Nevertheless, their melting values and solubility in toluene, chloroform, and THF indicated that these polymers probably were syndiotactic polystyrene. The ¹³C-NMR spectra of polystyrenes produced by complex **3a** and complexes **4a–4c** showed their characters of perfect syndiotacticity, which were also verified by the melting values close to 270 °C.

CONCLUSIONS

A series of rare-earth metal bis(alkyl) complexes incorporating pyridyl methylene cyclopentadienyl, indenyl, and fluorenyl derivatives were synthesized. The activities of these rare-earth metal catalysts in styrene polymerization depend strongly on both pyridyl and cyclopentadienyl derivative segments. Introducing electron-withdrawing group on indenyl ring can indeed enhance catalyst's activity. However, for the rare-earth metal catalysts bearing pyridyl methylene fluorenyl ligands, both scandium-based catalysts supported by electron-withdrawing (phenyl ring)^[19] and electron-donating groups (^tBu) modified ligands show much higher catalytic activity, and only electron-donating groups (^tBu) modified lutetium and yttrium analogues could initiate styrene polymerization with much higher activities. These facts demonstrated that the electronic effects on the catalyst's activity are very complicated and much more detailed work is needed to procure a deeper insight into the real relationship between catalyst's behaviour and its coordination environment. Further modification of these systems to explore their catalytic performance is underway.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2209-0>.

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