

# Rare-Earth-Metal–Hydrocarbyl Complexes Bearing Linked Cyclopentadienyl or Fluorenyl Ligands: Synthesis, Catalyzed Styrene Polymerization, and Structure–Reactivity Relationship

Zhongbao Jian,<sup>[a, b]</sup> Dongmei Cui,<sup>\*[a]</sup> and Zhaomin Hou<sup>\*[c]</sup>

**Abstract:** A series of rare-earth-metal–hydrocarbyl complexes bearing N-type functionalized cyclopentadienyl (Cp) and fluorenyl (Flu) ligands were facilely synthesized. Treatment of [Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(thf)<sub>2</sub>] with equimolar amount of the electron-donating aminophenyl-Cp ligand C<sub>5</sub>Me<sub>4</sub>H-C<sub>6</sub>H<sub>4</sub>-o-NMe<sub>2</sub> afforded the corresponding binuclear monoalkyl complex [(C<sub>5</sub>Me<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-o-NMe(μ-CH<sub>2</sub>))Y{CH<sub>2</sub>SiMe<sub>3</sub>}<sub>2</sub>] (**1a**) via alkyl abstraction and C–H activation of the NMe<sub>2</sub> group. The lutetium bis(allyl) complex [(C<sub>5</sub>Me<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-o-NMe<sub>2</sub>)Lu(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>] (**2b**), which contained an electron-donating aminophenyl-Cp ligand, was isolated from the sequential metathesis reactions of LuCl<sub>3</sub> with (C<sub>5</sub>Me<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-o-NMe<sub>2</sub>)Li (1 equiv) and C<sub>3</sub>H<sub>5</sub>MgCl (2 equiv). Following a similar procedure, the yttrium- and scandium-bis(allyl) com-

plexes, [(C<sub>5</sub>Me<sub>4</sub>-C<sub>5</sub>H<sub>4</sub>N)Ln(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>] (Ln = Y (**3a**), Sc (**3b**)), which also contained electron-withdrawing pyridyl-Cp ligands, were also obtained selectively. Deprotonation of the bulky pyridyl-Flu ligand (C<sub>13</sub>H<sub>9</sub>-C<sub>5</sub>H<sub>4</sub>N) by [Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(thf)<sub>2</sub>] generated the rare-earth-metal–dialkyl complexes, [(η<sup>3</sup>-C<sub>13</sub>H<sub>8</sub>-C<sub>5</sub>H<sub>4</sub>N)Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(thf)] (Ln = Y (**4a**), Sc (**4b**), Lu (**4c**)), in which an unusual asymmetric η<sup>3</sup>-allyl bonding mode of Flu moiety was observed. Switching to the bidentate yttrium–trisalkyl complex [Y(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-o-NMe<sub>2</sub>)<sub>3</sub>], the same reaction conditions afforded the corresponding yttrium bi-

s(aminobenzyl) complex [(η<sup>3</sup>-C<sub>13</sub>H<sub>8</sub>-C<sub>5</sub>H<sub>4</sub>N)Y(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-o-NMe<sub>2</sub>)<sub>2</sub>] (**5**). Complexes **1–5** were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR and X-ray spectroscopy, and by elemental analysis. In the presence of both [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and Al*i*Bu<sub>3</sub>, the electron-donating aminophenyl-Cp-based complexes **1** and **2** did not show any activity towards styrene polymerization. In striking contrast, upon activation with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] only, the electron-withdrawing pyridyl-Cp-based complexes **3**, in particular scandium complex **3b**, exhibited outstanding activity to give perfectly syndiotactic (*rrrr* > 99%) polystyrene, whereas their bulky pyridyl-Flu analogues (**4** and **5**) in combination with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and Al*i*Bu<sub>3</sub> displayed much-lower activity to afford syndiotactic-enriched polystyrene.

**Keywords:** cyclopentadienyl ligands • hydrocarbyl complexes • ligand effects • polymerization • rare-earth metals

## Introduction

The past two decades have witnessed tremendous growth in the number of reported rare-earth-metal–hydrocarbyl complexes, owing to their advantages in polymerization catalysis

and other related catalytic transformations, such as olefin hydrosilylation and hydroamination.<sup>[1]</sup> The hydrocarbyl complexes that contain linked- or unlinked monocyclopentadienyl (Cp) ligands and their derivatives have garnered an upsurge in interest because of their unique catalytic activities and selectivities for the (co-)polymerizations of simple olefins (such as ethylene), α-olefins, 1,3-conjugated dienes, styrene, etc.<sup>[1b,2]</sup> In general, the rare-earth-metal–hydrocarbyl complexes reported to date contain σ(η<sup>1</sup>)-alkyl and π-η<sup>3</sup>-allyl groups. In the cases of those containing σ(η<sup>1</sup>)-alkyl groups, such as CH<sub>3</sub>,<sup>[3]</sup> CH<sub>2</sub>Ph,<sup>[4]</sup> CH<sub>2</sub>SiMe<sub>2</sub>Ph,<sup>[5]</sup> and the extensively used CH<sub>2</sub>SiMe<sub>3</sub>,<sup>[1b,6]</sup> Lewis basic ligands, such as Et<sub>2</sub>O, THF, or DME (dimethoxyethane), are usually incorporated into the molecule to stabilize the highly unsaturated Lewis acidic rare-earth-metal centers. However, this strong Lewis base coordination hampers the access of olefin monomers to the active metal sites and severely decreases its activity. Recently, *ortho*-*N,N*-dimethylaminobenzyl (CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-*o*) has been reported as an efficient alternative to its above-mentioned alkyl counterparts, as it can serve as a bidentate ligand for rare-earth metal ions by forming chelating bonds through both its benzyl and amino

[a] Z. Jian, Prof. Dr. D. Cui  
State Key Laboratory of Polymer Physics and Chemistry  
Changchun Institute of Applied Chemistry  
Chinese Academy of Sciences, 5625 Renmin Street  
Changchun 130022 (P. R. China)  
Fax: (+86) 431-526-2774  
E-mail: dmcui@ciac.jl.cn

[b] Z. Jian  
Graduate School of the Chinese Academy of Sciences  
Beijing 100039 (P. R. China)

[c] Prof. Dr. Z. Hou  
Organometallic Chemistry Laboratory  
RIKEN Advanced Science Institute, Hirosawa 2–1 Wako  
Saitama 3510198 (Japan)  
Fax: (+81) 48-4624665  
E-mail: hou@riken.jp

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201102682>.

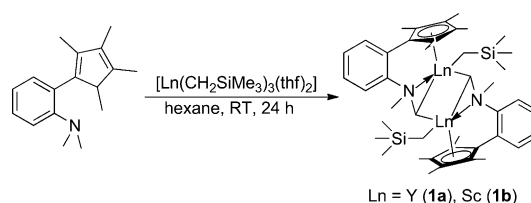
groups, and can therefore lead more easily to the formation of external Lewis-base-free complexes, although its reactivity is usually weaker than its above-mentioned alkyl counterparts.<sup>[7]</sup> Meanwhile, to balance the stability and reactivity,  $\pi$ - $\eta^3$ -allyl ligands, such as  $\text{CH}_2\text{C}(\text{Me})=\text{CH}_2$ ,<sup>[8]</sup>  $\text{CH}(\text{SiMe}_3)\text{CH}=\text{CH}(\text{SiMe}_3)$ ,<sup>[9]</sup> and the often-used  $\text{CH}_2\text{CH}=\text{CH}_2$ ,<sup>[10]</sup> have been employed to prepare solvent-free rare-earth-metal-allyl complexes that offer higher stabilities and appropriate activities.

On the other hand, syndiotactic polystyrene (sPS), first prepared by Ishihara et al. using a Cp-based titanium catalyst,<sup>[11]</sup> is a promising thermoplastic that has potential applications in engineering plastics because of its high melting point, high tensile modulus, and excellent physical properties.<sup>[12]</sup> Hitherto, a large number of titanium analogues of the general formula  $[\text{Cp}'\text{TiX}_3]$  ( $\text{Cp}'$ =substituted Cp, X=halogen or alkoxy),  $[\text{IndTiX}_3]$  (Ind=indenyl), or  $[\text{FluTiX}_3]$  (Flu=fluorenyl) have been reported that exhibit obvious improvements in both catalytic activity and syndiospecificity for styrene polymerization.<sup>[13]</sup> Comparatively, rare-earth-metal catalysts usually showed lower activities and less control over the specific selective styrene polymerization, although some unlinked Cp', hetero-Cp', Ind', or Flu-CMe<sub>2</sub>-Cp-based lanthanide- $\sigma$ -alkyl or -aminobenzyl complexes,<sup>[6n,7c,f,14]</sup> Ln- $\pi$ -allyl complexes,<sup>[10c,f]</sup> or Ln-BH<sub>4</sub> complexes<sup>[15]</sup> have been reported as efficient catalysts for the syndiospecific polymerization of styrene. However, so far the constrained geometry configuration (CGC) of rare-earth-metal catalysts have been less explored for the syndiospecific styrene polymerization.<sup>[16]</sup> In particular, studies on the structure-catalytic performance relationships remain scarce.<sup>[10c,14a]</sup>

Herein, we report the synthesis of a series of new N-type linked Cp- and Flu-ligated rare-earth-metal-alkyl, metal-aminobenzyl, and metal-allyl complexes by using salt metathesis procedures or the acid-base approach. Upon activation with cocatalysts, all of these complexes displayed distinct catalytic behaviors towards the polymerization of styrene, among which the catalyst based on the (pyridyl-Cp)-scandium-bis(allyl) precursor exhibited notable activity and perfect syndiospecificity (*rrrr* >99%) to afford pure sPS. All of these complexes were fully characterized by NMR spectroscopy and X-ray diffraction analysis, which revealed structural characteristics, such as dimerization, bite angle, solvent coordination, and the coordination modes of the ligands. Based on these data, we have established the relationship between these factors (the steric hindrance around the central metal, the electron-donating or -withdrawing effect, the coordination mode of the ancillary ligand, and the Lewis acidity of the central metal) and the catalytic activity and syndiospecificity, which might shed new light on the design of more-efficient catalysts and further investigation of the reaction mechanism.

## Results and Discussion

**Preparation of alkyl complexes 1a and 1b:** In general, rare-earth-metal-alkyl complexes can be prepared by sequential metathesis reactions between alkaline ligand salts and rare-earth-metal trichlorides followed by reaction with alkyl lithium reagents, or through alkyl abstraction of rare-earth-metal-tris(alkyl) compounds by neutral ligands. Compared with the multistep synthesis of compound **1b** reported previously,<sup>[17]</sup> the simple alkyl-abstraction method, which involved the treatment of  $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$  with 1 equivalent of electron-donating aminophenyl-Cp ligand  $\text{C}_5\text{Me}_4\text{H}-\text{C}_6\text{H}_4-o\text{-NMe}_2$  at room temperature, afforded the binuclear monoalkyl complexes  $[(\{\text{C}_5\text{Me}_4\text{-C}_6\text{H}_4-o\text{-NMe}(\mu\text{-CH}_2)\})\text{Ln}\{\text{CH}_2\text{SiMe}_3\}_2]$  (Ln=Y (**1a**), Sc (**1b**)) in much higher yields, in which the C-H activation of the aminomethyl group took place simultaneously (Scheme 1). The C-H activation of



Scheme 1. Synthesis of alkyl complexes **1a** and **1b**.

$\text{NMe}_2$  was confirmed by the presence of two doublet resonances ( $\delta \approx 1.52$  and  $1.93$  ppm) in the <sup>1</sup>H NMR spectrum of compound **1a**, which were assigned to the newly formed NCH<sub>2</sub> groups; these resonances were correlated to those at  $\delta = 1.44$  ppm and  $\delta = 1.54$  ppm in compound **1b**.<sup>[17]</sup> The analogous C-H activation of  $\text{NMe}_2$  has been observed previously when the reaction of a multidentate Cp' ligand with  $\text{ScCl}_3$  and  $\text{LiCH}_2\text{SiMe}_3$  was performed at high temperature ( $70^\circ\text{C}$ ) over 6 days.<sup>[18]</sup> Thus, to confirm whether the reaction temperature prompted the C-H activation of the  $\text{NMe}_2$  group in our case, the acid-base reaction was performed at 0 or  $-20^\circ\text{C}$ ; at both temperatures, we still observed the selective formation of the same binuclear monoalkyl products.

Therefore, we believed that the C-H activation of the  $\text{NMe}_2$  group in this CGC ligand was unavoidable. X-ray analysis revealed that complex **1a** had a dimeric structure, with  $C_2$  symmetry at the center of the molecule (Figure 1). Two carbon atoms (C17 and C17A), two yttrium atoms, and two nitrogen atoms formed a six-membered ring that was planar to within  $0.073 \text{ \AA}$ ; this planarity was in striking contrast to the heavily crooked six-membered ring in compound **1b**.<sup>[17]</sup> Moreover, the  $\text{Cp}_{\text{cent}}\text{-Y1-N1}$  bite angle ( $96.7(3)^\circ$ ) in compound **1a** was slightly larger than in the corresponding  $[(\text{C}_5\text{Me}_4\text{-C}_6\text{H}_4-o\text{-NMe}_2)\text{Y}(\eta^3\text{-C}_3\text{H}_5)_2]$  complex ( $95.4(3)^\circ$ ).<sup>[10a]</sup> Similarly, the  $\text{Cp}_{\text{cent}}\text{-Sc1-N1}$  bite angle in compound **1b** was as large as  $101.5^\circ$ .<sup>[17]</sup> Not unexpectedly, there was a marked difference in the Y1-N1 bond lengths in compounds **1a** and  $[(\text{C}_5\text{Me}_4\text{-C}_6\text{H}_4-o\text{-NMe}_2)\text{Y}(\eta^3\text{-C}_3\text{H}_5)_2]$ <sup>[10a]</sup> ( $2.389(2)$  and  $2.630(2) \text{ \AA}$ , respectively), which was a consequence of metal-



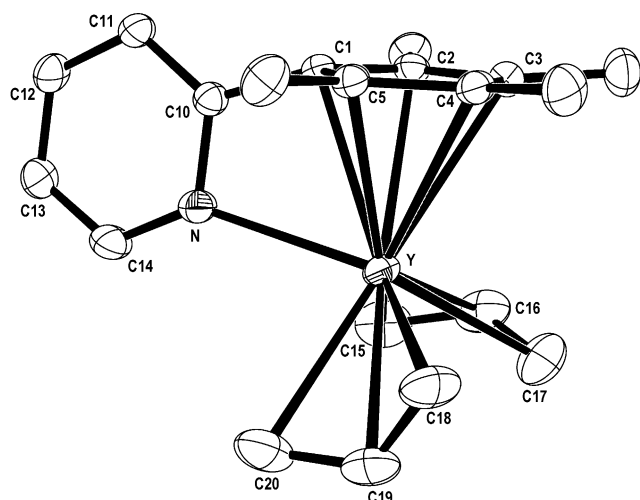


Figure 3. X-ray structure of compound **3a**. Thermal ellipsoids set at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y–C<sub>Cp</sub> (average) 2.659(2), Y–C<sub>Pcent1</sub> 2.370(2), Y–C<sub>AT</sub> (average) 2.600(3), Y–C<sub>AC</sub> (average) 2.617(3), Y–N 2.510(2); C<sub>AT</sub>–C<sub>AC</sub>–C<sub>AT</sub> 126.8(3), C<sub>Pcent1</sub>–Y–C<sub>cent2</sub> 112.7(6), C<sub>Pcent1</sub>–Y–C<sub>cent3</sub> 132.1(1), C<sub>cent2</sub>–Y–C<sub>cent3</sub> 107.9(2), C<sub>Pcent1</sub>–Y–N 82.7(6). C<sub>AT</sub>=terminal allylic carbon atom; C<sub>AC</sub>=central allylic carbon atom; C<sub>Pcent1</sub>, C<sub>cent2</sub>, and C<sub>cent3</sub> are the centroids of the cyclopentadienyl ring and the two allyl ligands, respectively.

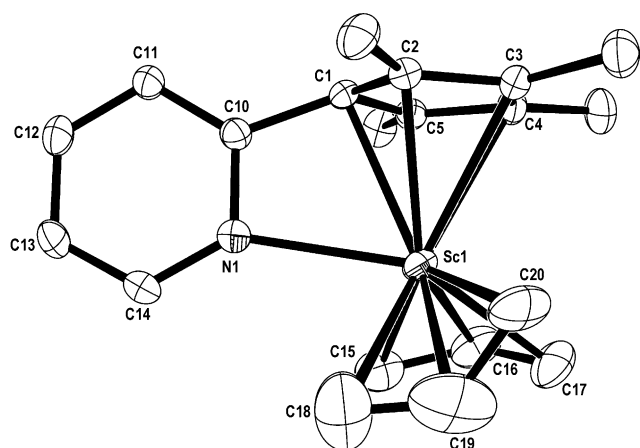
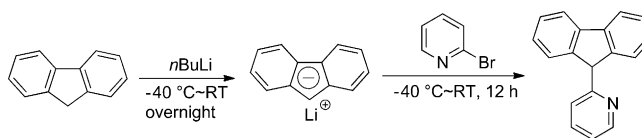


Figure 4. X-ray structure of compound **3b**. Thermal ellipsoids set at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sc1–C<sub>Cp</sub> (average) 2.523(3), Sc1–C<sub>Pcent1</sub> 2.118(2), Sc1–C<sub>AT</sub> (average) 2.483(4), Sc1–C<sub>AC</sub> (average) 2.476(4), Sc1–N1 2.393(3); C<sub>AT</sub>–C<sub>AC</sub>–C<sub>AT</sub> 129.1(5), C<sub>Pcent1</sub>–Sc1–C<sub>cent2</sub> 114.2(6), C<sub>Pcent1</sub>–Sc1–C<sub>cent3</sub> 131.7(9), C<sub>cent2</sub>–Sc1–C<sub>cent3</sub> 106.9(6), C<sub>Pcent1</sub>–Sc1–N1 86.6(1). C<sub>AT</sub>=terminal allylic carbon atom; C<sub>AC</sub>=central allylic carbon atom; C<sub>Pcent1</sub>, C<sub>cent2</sub>, and C<sub>cent3</sub> are the centroids of the cyclopentadienyl ring and the two allyl ligands, respectively.

protons (methine) gave a quintet at around  $\delta \approx 6.34$ – $6.43$  ppm, whilst the terminal allylic protons (methylene, H<sub>anti</sub> and H<sub>syn</sub>) exhibited two doublets at  $\delta \approx 2.94$  and  $3.21$  ppm, thus suggesting a slow exchange of the *anti* and *syn* protons in solution, which was different from the single doublets of methylene protons observed in [(C<sub>5</sub>Me<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-*o*-NMe<sub>2</sub>)Y(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>]<sup>[10a]</sup> and [(C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Y(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>-(thf)].<sup>[10b]</sup> By contrast, the allyl moieties in complex **3b** ap-

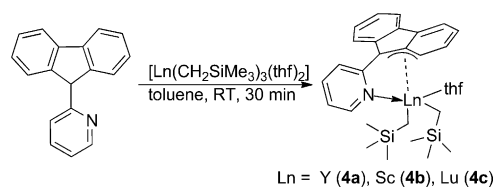
peared as a quintet at  $\delta \approx 6.10$ – $6.16$  ppm for the methine protons but only as one doublet at  $\delta = 3.27$  ppm for the equivalent *anti* and *syn* protons, which was different from the two broad singlets of the methylene protons in the unlinked-Cp–scandium–allyl complex [(C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>].<sup>[8a]</sup> The bond lengths between the Y<sup>III</sup> atom and the terminal allyl carbons in compound **3a** (Y–C<sub>AT</sub>; average 2.600(3) Å) were shorter than those between the Y<sup>III</sup> atom and the central allyl carbon atoms (Y–C<sub>AC</sub>; average 2.617(3) Å). In contrast, the average bond length between the Sc<sup>III</sup> center and the terminal carbon atoms of the allyl groups (Sc1–C<sub>AT</sub>; average 2.483(4) Å) in complex **3b** was comparable to that between the Sc<sup>III</sup> atom and the central carbon atoms of the allyl groups (Sc1–C<sub>AC</sub>; average 2.476(4) Å); both distances were slightly longer than the corresponding distances in [(C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>] (Sc–C<sub>AT</sub>: 2.445(5) Å; Sc–C<sub>AC</sub>: 2.441(6) Å).<sup>[8a]</sup> The C<sub>Pcent1</sub>–Y–N 82.7(6)° bite angle in complex **3a** was much smaller than in complex **2a** (95.4(3)°), thus suggesting a more-open environment around the Y<sup>III</sup> ion in complex **3a**. This open environment was also demonstrated by the Y–C<sub>Pcent</sub> distances: **3a** (2.370(2)) > **2a** (2.349(2)) > **1a** (2.347(2)). Similarly, the C<sub>Pcent1</sub>–Sc1/Lu1–N1 bite angles in complexes **3b** and **3c** were only 86.6(1)° and 84.1(3)°, respectively. The environments of the openings of complexes **3a–3c** could contribute significantly to their high activities towards the polymerization of bulky styrene monomer (see below).

**Preparation of complexes 4a–4c:** To further study the effect of steric hindrance, the pyridyl-modified fluorene compound C<sub>13</sub>H<sub>9</sub>-C<sub>5</sub>H<sub>4</sub>N, a more-bulky ligand, was designed and prepared by the treatment of fluorene with butyllithium at –40 °C and subsequent reaction with 2-bromopyridine at room temperature (Scheme 4). The <sup>1</sup>H NMR spectrum of



Scheme 4. Synthesis of ligand C<sub>13</sub>H<sub>9</sub>-C<sub>5</sub>H<sub>4</sub>N.

the ligand displayed a signal in the upfield region ( $\delta = 5.60$  ppm), which was assigned to the nonconjugated Flu protons. The straightforward protonolysis reaction of this ligand with [Ln(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(thf)<sub>2</sub>] in toluene selectively generated alkyl complexes **4a–4c** (Scheme 5). The <sup>1</sup>H NMR



Scheme 5. Synthesis of alkyl complexes **4a–4c**.

spectra of compounds **4a–4c** differentiated at the resonances for the Ln-CH<sub>2</sub>SiMe<sub>3</sub> protons, which appeared as a doublet ( $\delta = -0.31$  ppm) and as two singlets ( $\delta = 0.20$  and  $-0.54$  ppm), respectively. Complexes **4a–4c** gave similar topologies for the eight Flu H protons (which appeared as four peaks in each case), thus indicating an asymmetric coordination mode of the Flu ligands around the central metal atoms. Complexes **4a–4c** were characterized by X-ray diffraction analysis as monomeric bis(alkyl) complexes with ligated thf molecules, wherein the Flu moieties were bound to the central metal atoms in an asymmetric  $\eta^3$ -allyl fashion (Figure 5). Because of the similar structures of **4a–4c**,

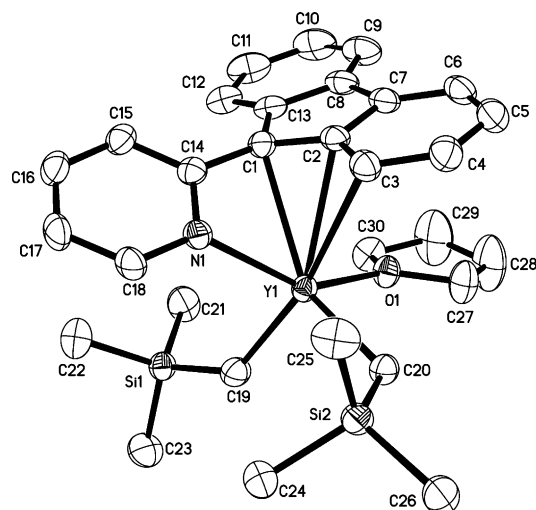
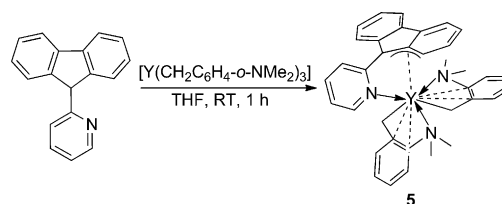


Figure 5. X-ray structure of compound **4a**. Thermal ellipsoids set at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–C1 2.689(2), Y1–C2 2.755(2), Y1–C3 2.916(2), Y1–C19 2.339(2), Y1–C20 2.365(2), Y1–N1 2.4086(19); C20–C19–Y1 88.5(3), C29–C28–Y1 86.1(3), C19–Y1–C1 117.72(8), C20–Y1–C1 137.49(8), C19–Y1–N1 96.21(8), C20–Y1–N1 111.17(8), N1–Y1–C1 55.27(7).

herein, we selected compound **4a** as a representative for discussion. The Y1–C1 bond length in complex **4a** (2.689(2) Å) fell within the typical range for Y–Cp<sub>Flu</sub> bond lengths (2.56(2)–2.74(2) Å),<sup>[19]</sup> much shorter than Y1–C2 (2.755(2) Å) and Y1–C3 (2.916(2) Å), thus suggesting that the  $\eta^3$ -allyl bonding mode slipped more toward the central five-membered ring than the six-membered ring.<sup>[19a]</sup> Furthermore, the dihedral angle between the pyridyl-based plane (C14–C18 and N1) and the Flu-based plane (C1–C13) in compound **4a** (34.41°) also confirmed the tendency of the Flu moiety towards an asymmetric  $\eta^3$ -allyl bonding mode. To the best of our knowledge, to date there have been various reported bonding modes of the Flu moiety in lanthanidocenes and zirconocenes, as established by X-ray diffraction analysis: the typical symmetric  $\eta^5$  mode in  $[(\eta^5:\eta^5\text{-CpSiMe}_2\text{Flu})\text{Y}[\text{N}(\text{SiMe}_3)_2]]$ ,<sup>[20]</sup> the symmetric  $\eta^3$ -bonding mode in  $[(\eta^5:\eta^3\text{-Flu})_2\text{Sm}(\text{thf})_2]$ <sup>[21]</sup> and  $[(\eta^5:\eta^3\text{-CpSiMe}_2\text{Flu})\text{YCl}_2\text{Li}(\text{OEt})_2]$ ,<sup>[19]</sup> the exocyclic  $\eta^1(\eta^2)$  coordination mode in the anionic complex  $[(\eta^3:\eta^5\text{-FluC-}$

$\text{Me}_2\text{Cp})(\eta^1:\eta^5\text{-FluCMe}_2\text{Cp})\text{Y}]^-\text{[Li}(\text{Et}_2\text{O})(\text{thf})_3]^+$ ,<sup>[19b]</sup> and the symmetric  $\eta^1$  mode in  $[(\eta^5\text{-C}_5\text{H}_4\text{Me})_2\text{Zr}(\eta^1\text{-Flu})(\text{Cl})]$ .<sup>[22]</sup> As such, the asymmetric  $\eta^3$ -allyl bonding mode of Flu moieties in compounds **4a–4c** is rare, although it has been observed in a few Flu-based complexes.<sup>[19]</sup>

**Preparation of complex 5:** The acid-base reaction between the yttrium–tris(aminobenzyl) compound  $[\text{Y}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3]$  and 1 equivalent of C<sub>13</sub>H<sub>9</sub>-C<sub>5</sub>H<sub>4</sub>N in THF at room temperature afforded the corresponding yttrium–bis(aminobenzyl) complex **5** in 59% yield (Scheme 6). NMR spectro-



Scheme 6. Synthesis of aminobenzyl complex **5**.

scopic analysis of compound **5** revealed that the methylene protons of the metal–aminobenzyl Y–CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*o*-NMe<sub>2</sub> moieties gave a broad singlet at  $\delta = 1.36$  ppm.<sup>[7b,d]</sup> No resonances from the THF molecules were detected, thereby confirming the absence of solvent coordination. X-ray diffraction analysis confirmed the molecular structure of complex **5** as a THF-free monomer (Figure 6). The ligands were bound to the central metal atom in an  $\eta^3$ -allyl/ $\kappa^1$  bonding mode with Y1–C1, Y1–C2, Y1–C3, and Y1–N1 bond lengths of 2.689(2), 2.755(2), 2.916(2), and 2.4086(19) Å, respectively,

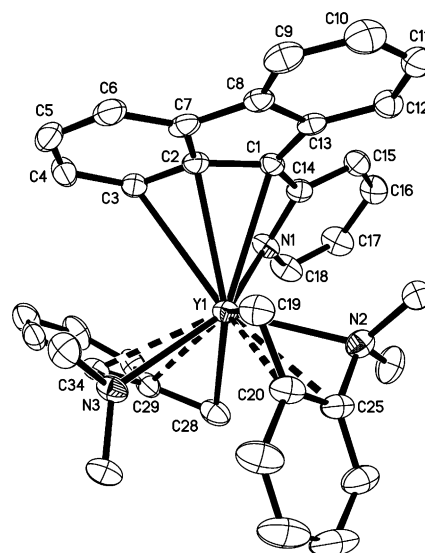


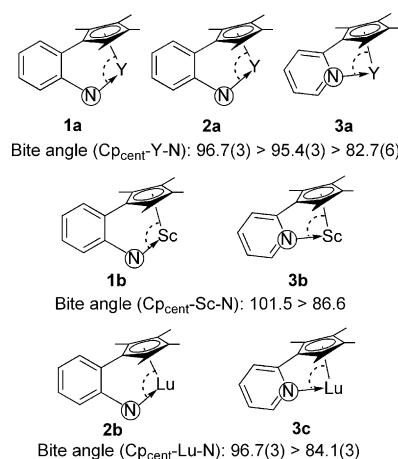
Figure 6. X-ray structure of compound **5**. Thermal ellipsoids set at 40% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1–C1 2.836(4), Y1–C2 2.776(5), Y1–C3 2.944(5), Y1–C19 2.427(5), Y1–C20 2.800(5), Y1–C25 2.851(5), Y1–C28 2.468(5), Y1–C29 2.774(5), Y1–C34 2.808(5), Y1–N1 2.438(4), Y1–N2 2.533(4), Y1–N3 2.545(4); C20–C19–Y1 88.5(3), C29–C28–Y1 86.1(3).

which were comparable to those observed in alkyl complexes **4a–4c**. Both aminobenzyl ligands chelated to the central metal atom through the benzyl methylene carbon atoms and the amino nitrogen atoms in bidentate modes. Interactions between the Y center and the four phenyl atoms (*ipso* and *ortho*) of the benzyl groups (Y1–C20, 2.800(5) Å; Y1–C25, 2.851(5) Å; Y1–C29, 2.774(5) Å; Y1–C34, 2.808(5) Å) were observed in compound **5**. Such interactions have been observed in cationic aminobenzyl scandium complexes<sup>[7c,e]</sup> but were absent in PNP-based yttrium-bis(aminobenzyl) complexes, where the bond lengths of the Y–C (*ipso* and *ortho* phenyl carbon atoms) were in the range 3.137–3.328 Å.<sup>[7b]</sup> Because of this interaction, the C20–C19–Y1 and C29–C28–Y1 angles (88.5(3)° and 86.1(3)°, respectively) were significantly smaller than those in the PNP-type yttrium-bis(aminobenzyl) compounds (108.8(2)° and 103.5(2)°, respectively).<sup>[7b]</sup>

**Styrene polymerization:** It has been reported that lanthanide-hydrocarbyl complexes containing Ln-σ-C or Ln-π-C bonds with appropriate ancillary ligands displayed good activity for styrene polymerization to provide aPS (atactic polystyrene), sPS (syndiotactic polystyrene), or iPS (isotactic polystyrene). Herein, we will systematically explore the styrene polymerization catalyzed by all of the above-synthesized precursors upon activation with co-catalysts in toluene at room temperature (Table 1).

First, we selected complexes **1** and **2**, which contained electron-donating aminophenyl-Cp ligands, as the objects of our study. Unfortunately, upon activation with 1 equivalent of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], the electron-donating aminophenyl-Cp-yttrium/scandium-alkyl complexes (**1a** and **1b**) did not show any activity towards styrene polymerization, either in the presence or absence of 10 equivalents of Al*i*Bu<sub>3</sub> (Table 1, runs 1 and 2, respectively). Under the same conditions, the electron-donating aminophenyl-Cp-yttrium/lutetium-allyl complexes (**2a** and **2b**) were also inert for the

polymerization of styrene (Table 1, runs 3 and 4, respectively). We deduced that the large bite angle (96.7°–101.5°) of complexes **1** and **2** afforded crowded environments around the central metal atoms (Scheme 7), which hampered the coordination and insertion of the bulky styrene monomer. Furthermore, the electron-donating effect of the amino-phenyl-Cp ligand also decreased the Lewis acidity of the central metal atom, which weakened the coordination ability of the metal center. Therefore, to confirm the electronic effects and the effect of the bite angle, the electron-withdrawing pyridyl-Cp-stabilized allyl complexes **3a–3c**, which contained much-smaller bite angles (82.7–86.6°), were explored for styrene polymerization. To our delight, in combination with only 1 equivalent of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], the electron-withdrawing pyridyl-Cp-yttrium-allyl complex (**3a**) showed moderate activity to give syndiotactic-enriched PS (*rrrr* = 88%); the activity increased when the reaction was performed in chlorobenzene, albeit with a loss in the specific selectivity (Table 1, runs 5 and 6). More remarkably, the more Lewis acidic scandium analogue (**3b**) demonstrated



Scheme 7. Bite angles of complexes **1–3**.

Table 1. Polymerization of styrene (St) catalyzed by complexes **1a**, **1b**, **2a**, **2b**, **3a–3c**, **4a–4c**, and **5**.<sup>[a]</sup>

Run	Cat.	AlR <sub>3</sub>	[St]/[Ln]	<i>t</i> [min]	Conv. [%]	Activity <sup>[b]</sup>	sPS <sup>[c]</sup> [%]	<i>M<sub>n</sub></i> <sup>[d]</sup> (× 10 <sup>-4</sup> )	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>[d]</sup>	<i>T<sub>m</sub></i> <sup>[e]</sup> [°C]
1	<b>1a</b> (Y)	Al <i>i</i> Bu <sub>3</sub>	500	120	trace					
2	<b>1b</b> (Sc)	Al <i>i</i> Bu <sub>3</sub>	500	120	trace					
3	<b>2a</b> (Y)	Al <i>i</i> Bu <sub>3</sub>	500	120	trace					
4	<b>2b</b> (Lu)	Al <i>i</i> Bu <sub>3</sub>	500	120	trace					
5	<b>3a</b> (Y)		500	50	20	13	88	4.6	2.50	266
6 <sup>[f]</sup>	<b>3a</b> (Y)		1000	30	>99	178	0	0.8	2.84	n.d.
7	<b>3b</b> (Sc)		500	1	>99	3120	>99	14.4	1.40	271
8	<b>3b</b> (Sc)		1000	1	>99	6240	>99	26.3	1.50	271
9 <sup>[g]</sup>	<b>3b</b> (Sc)		500	60	trace					
10 <sup>[f]</sup>	<b>3b</b> (Sc)		1000	30	>99	178	0	1.0	3.88	n.d.
11 <sup>[h]</sup>	<b>3c</b> (Lu)		500	1	>99	3120	>99	9.7	1.94	270
12	<b>4a</b> (Y)	Al <i>i</i> Bu <sub>3</sub>	500	360	5	0.4	n.d.	n.d.	n.d.	n.d.
13	<b>4b</b> (Sc)	Al <i>i</i> Bu <sub>3</sub>	500	360	48	4	85	1.5	1.84	260
14	<b>4c</b> (Lu)	Al <i>i</i> Bu <sub>3</sub>	500	360	19	1.6	81	1.0	2.23	256
15	<b>5</b> (Y)	Al <i>i</i> Bu <sub>3</sub>	500	360	13	1.0	76	1.1	1.92	251

[a] Polymerization conditions: [Ln] (10 μmol), [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (10 μmol), Al*i*Bu<sub>3</sub> (100 μmol), toluene/monomer = 5:1 (v/v), *T<sub>p</sub>* = 20 °C, unless otherwise noted. [b] Given in kg mol<sup>-1</sup> h<sup>-1</sup>. [c] Measured by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy in [D<sub>2</sub>]1,2-dichlorobenzene at 125 °C. [d] Determined by GPC in 1,2,4-trichlorobenzene at 150 °C against a polystyrene standard. [e] Determined by DSC. [f] Chlorobenzene (5 mL). [g] [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (10 μmol). [h] Ref. [16a].

excellent activity ( $3.12 \times 10^3 \text{ kg mol}_{\text{sc}}^{-1} \text{ h}^{-1}$ ) for the polymerization of styrene, affording perfect sPS ( $r_{\text{rrrr}} > 99\%$ ) with high molecular weight and narrow molecular-weight distribution ( $M_w/M_n = 1.40$ ), thus denoting a single-site behavior of the catalytic system (Table 1, run 7). Furthermore, increasing the styrene loading from 500 to 1000 equivalents afforded an activity of up to  $6.24 \times 10^3 \text{ kg mol}_{\text{sc}}^{-1} \text{ h}^{-1}$ , which was comparable to the most-active scandium systems reported so far.<sup>[6n,14a]</sup> The resultant PS remained purely syndiotactic (Table 1, run 8), as confirmed by the strong, sharp singlets at  $\delta = 145.67 \text{ ppm}$  (*ipso*-Ph), 45.04 ppm (methylene), and  $\delta = 41.67 \text{ ppm}$  (methine) in the  $^{13}\text{C}$  NMR spectrum, and by the strong endothermic peak at 271 °C in the DSC curve (see the Supporting Information). Surprisingly, in the presence of  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$  instead of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ , scandium analogue **3b** did not show any activity for the polymerization of styrene (Table 1, run 9). When the solvent was changed to chlorobenzene, scandium analogue **3b** showed a lower activity, thereby affording atactic PS (Table 1, run 10). Like compound **3b**, lutetium precursor **3c** also exhibited good activity, and gave perfect sPS (Table 1, run 11). Therefore, these complexes, which contain a more-open environment around the central metal atom (smaller bite angle), an electron-withdrawing ancillary ligand, and a more Lewis acidic central metal atom, are conducive to the polymerization of bulky styrene.<sup>[10c]</sup>

Intrigued by these notable results for complexes **3a–3c**, which had  $\eta^5$ -coordination modes of the Cp moieties, the catalysis of pyridyl-functionalized Flu-alkyl complexes **4a–4c**, which contained asymmetric  $\eta^3$ -allyl bonding modes of the Flu moieties, were also explored to determine if the coordination mode of the ancillary ligands had an influence on the activity and selectivity of the styrene polymerization. Upon activation with only 1 equivalent of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ , the THF-solvated precursors **4a–4c**, which contained asymmetric  $\eta^3$ -allyl bonding modes, could not initiate the polymerization of styrene, even though they possessed the more active Ln- $\sigma$ -CH<sub>2</sub>SiMe<sub>3</sub> bond. By adding 10 equivalents of Al*i*Bu<sub>3</sub> to the above catalytic system, styrene was successfully polymerized in a much-lower activity to afford syndiotactic-enriched PS ( $r_{\text{rrrr}} = 81\text{--}85\%$ ; Table 1, runs 12–14). Similarly, in the presence of 1 equivalent of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  and 10 equivalents of Al*i*Bu<sub>3</sub>, solvent-free complex **5**, which contained an asymmetric  $\eta^3$ -allyl bonding mode, also only showed low activity for the polymerization of styrene to give syndiotactic-enriched PS ( $r_{\text{rrrr}} = 76\%$ ; Table 1, run 15). These results revealed that, in view of both activity and selectivity, an  $\eta^5$ - $\pi$ -coordination mode of the ancillary ligand was superior to an asymmetric  $\eta^3$ -allyl bonding mode for styrene polymerization.<sup>[7c]</sup> This superiority may be because the asymmetric  $\eta^3$ -allyl bonding mode of the ancillary ligand blocks the electron delocalization, which reduces the electron-withdrawing effect of the ligand.

## Conclusion

We have synthesized and fully characterized a series of rare-earth-metal-hydrocarbyl complexes that contain N-type functionalized Cp and Flu ligands. Reaction of the electron-donating aminophenyl-Cp ligand with  $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$  promoted the C–H activation of the aminomethyl group, thereby leading to the formation of its binuclear monoalkyl counterparts. Both the electron-donating aminophenyl-Cp-based rare-earth-metal-bis(allyl) complexes and the electron-withdrawing pyridyl-Cp-based rare-earth-metal-bis(allyl) complexes were readily obtained by the one-pot metathetical reactions of LnCl<sub>3</sub> with lithium salts of the ligands and C<sub>3</sub>H<sub>5</sub>MgCl. The acid-base reaction between  $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$  or  $[\text{Y}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3]$  and the bulky pyridyl-modified fluorene ligand straightforwardly yielded the corresponding rare-earth-metal-bis(alkyl) or yttrium-bis(aminobenzyl) complexes with an unusual asymmetric  $\eta^3$ -allyl bonding mode of the Flu moiety. In the presence of activator, all of these complexes displayed distinct catalytic behaviors for the polymerization of styrene. These results reasonably suggested that such complexes, which contained a more-open environment around the central metal atom (small bite angle) and a more Lewis acidic central metal atom (bearing an electron-withdrawing ancillary ligand), facilitated the construction of a highly active catalyst system for styrene polymerization. Furthermore, both the more-sterically congested environment around the central metal atom and the  $\eta^5$ - $\pi$ -coordinated ancillary ligand contributed significantly to the specific selectivity. Thus, the combination of the electron-withdrawing pyridyl-Cp-based scandium-bis(allyl) complex, which had an  $\eta^5$ -coordination mode, and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  afforded the optimal catalyst system, which showed a notable activity to afford the perfect sPS ( $r_{\text{rrrr}} > 99\%$ ).

## Experimental Section

**General procedures and materials:** All reactions were carried out under a dry, oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBraun glovebox. All solvents were purified by an MBraun SPS system. Samples of rare-earth-metal-organic complexes for NMR spectroscopic measurements were prepared in the glovebox by using NMR tubes sealed by paraffin film. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV400 or AV600 spectrometer. Elemental analysis was performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). Toluene was distilled from sodium/benzophenone under nitrogen and degassed thoroughly prior to use. Styrene (Aldrich) was dried over CaH<sub>2</sub> under stirring for 48 h and distilled under reduced pressure before use. C<sub>3</sub>H<sub>5</sub>MgCl (2.0 M in THF) was purchased from Aldrich. The ligands C<sub>3</sub>Me<sub>4</sub>H-C<sub>6</sub>H<sub>4</sub>-*o*-NMe<sub>2</sub> and C<sub>3</sub>Me<sub>4</sub>H-C<sub>3</sub>H<sub>4</sub>N were prepared according to literature procedures.<sup>[23]</sup> Complexes  $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$ <sup>[24]</sup> and  $[\text{Y}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3]$ <sup>[7d]</sup> were synthesized as described previously. Organoborates  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  and  $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$  were synthesized according to literature procedures.<sup>[25]</sup>

**X-ray crystallographic studies:** Crystals suitable for X-ray analysis were obtained as described and were manipulated in a glovebox. Data collections were performed at  $-88.5^\circ\text{C}$  on a Bruker SMART APEX diffrac-

tometer with a CCD area detector, using graphite-monochromated Mo $\text{K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Determination of the crystal class and unit cell parameters was carried out by the SMART program package.<sup>[26]</sup> The raw frame data were processed using SAINT and SADABS to yield the reflection data file.<sup>[27]</sup> The structures were solved by using the SHELXTL program.<sup>[28]</sup> Refinement was performed on  $F^2$  anisotropically for all non-hydrogen 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.

**Synthesis of complex 1a:** *Path a:* To a solution of  $[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$  (0.495 g, 1.0 mmol) in *n*-hexane (5 mL), 1 equiv of  $\text{C}_5\text{Me}_4\text{H-C}_6\text{H}_4\text{-}o\text{-NMe}_2$  (0.241 g, 1.0 mmol in 5 mL *n*-hexane) was added dropwise at RT. The mixture was then stirred for 24 h. Removal of the volatile compounds gave a pale-yellow oily residue. The residue was dissolved with *n*-hexane (3 mL) and then cooled to  $-30^\circ\text{C}$  for 20 h to give a crystalline solid, which was washed carefully with a small amount of *n*-hexane and dried under vacuum to afford compound **1a** as a white powder (0.292 g, 68.0%). Single crystals for X-ray analysis grew from *n*-hexane over several days at  $-30^\circ\text{C}$ .  $^1\text{H NMR}$  (400 MHz,  $[\text{D}_6]$ benzene,  $25^\circ\text{C}$ ):  $\delta = -1.15$  (br s, 2H;  $\text{YCH}_2\text{SiMe}_3$ ),  $-0.75$  (br s, 2H;  $\text{YCH}_2\text{SiMe}_3$ ), 0.20 (s, 18H;  $\text{CH}_2\text{SiMe}_3$ ), 1.52 (d,  $^2J(\text{H,H}) = 12.0 \text{ Hz}$ , 2H;  $\text{NCH}_2$ ), 1.93 (d,  $^2J(\text{H,H}) = 12.2 \text{ Hz}$ , 2H;  $\text{NCH}_2$ ), 2.05 (s, 6H;  $\text{C}_5\text{Me}_4$ ), 2.07 (s, 6H;  $\text{C}_5\text{Me}_4$ ), 2.25 (s, 6H;  $\text{C}_5\text{Me}_4$ ), 2.41 (s, 6H;  $\text{C}_5\text{Me}_4$ ), 2.67 (s, 6H;  $\text{NMe}$ ), 7.09–7.29 ppm (m, 8H,  $\text{NC}_6\text{H}_4$ );  $^{13}\text{C NMR}$  (100 MHz,  $[\text{D}_6]$ benzene,  $25^\circ\text{C}$ ):  $\delta = 5.00$  (s, 3C;  $\text{CH}_2\text{SiMe}_3$ ), 5.34 (s, 3C;  $\text{CH}_2\text{SiMe}_3$ ), 10.96, 11.91, 12.03, 12.29, 12.38, 12.73, 12.78, 13.39 (s, 8C;  $\text{C}_5\text{Me}_4$ ), 33.62, 34.08 (s, 2C;  $\text{YCH}_2\text{SiMe}_3$ ), 45.75, 46.93 (s, 2C;  $\text{NMe}$ ), 73.15 (d,  $J(\text{Y,C}) = 29.1 \text{ Hz}$ , 1C;  $\text{NCH}_2$ ), 73.23 (d,  $J(\text{Y,C}) = 29.1 \text{ Hz}$ , 1C;  $\text{NCH}_2$ ), 114.97, 115.29, 121.74, 123.25, 123.64, 127.06, 127.30, 129.27, 129.33, 132.82, 134.27, 134.47, 159.31, 161.06 ppm ( $\text{C}_6\text{H}_4$  and  $\text{C}_5\text{Me}_4$ ); elemental analysis calcd (%) for  $\text{C}_{42}\text{H}_{64}\text{N}_2\text{Si}_2\text{Y}_2$ : C 60.71, H 7.76, N 3.37; found: C 60.24, H 7.51, N 3.25. *Path b:* Under a nitrogen atmosphere, *n*BuLi (1.6 M in *n*-hexane, 0.66 mL, 1.05 mmol) was added dropwise to a solution of  $\text{C}_5\text{Me}_4\text{H-C}_6\text{H}_4\text{-}o\text{-NMe}_2$  (0.241 g, 1.0 mmol) in THF (15 mL) at  $-78^\circ\text{C}$  and was stirred for 30 min. The solution was slowly warmed to RT and was left to react for another 12 h before being added to a suspension of  $\text{YCl}_3$  (0.195 g, 1.0 mmol) in THF (20 mL) at RT. The mixture was stirred for 4 h to afford a clear solution, to which  $\text{LiCH}_2\text{SiMe}_3$  (0.188 g, 2.0 mmol) was added. The resulting solution was stirred for 24 h. Removal of the volatile compounds yielded a residue, which was extracted with *n*-hexane. Evaporation of the solvent afforded compound **1a** as a white crystalline solid (0.236 g, 56.7%).

**Synthesis of complex 2b:** To a suspension of  $\text{LuCl}_3$  (0.281 g, 1.0 mmol) in THF (20 mL), 1 equiv of  $[\text{C}_5\text{Me}_4\text{-C}_6\text{H}_4\text{-}o\text{-NMe}_2]\text{Li}$  (0.247 g, 1.0 mmol) was slowly added at RT under a nitrogen atmosphere. The mixture was stirred for 4 h to afford a clear solution, to which  $\text{C}_3\text{H}_5\text{MgCl}$  (1.0 mL, 2.0 mmol, 2.0 M in THF) was added. The resulting light-yellow solution was stirring overnight. Removal of volatile compounds, extraction with toluene, and drying under vacuum gave compound **2b** as a yellow crystalline solid (0.288 g, 57.9%). Single crystals suitable for X-ray analysis were recrystallized from toluene/*n*-hexane.  $^1\text{H NMR}$  (600 MHz,  $[\text{D}_6]$ benzene,  $25^\circ\text{C}$ ):  $\delta = 1.93$  (s, 6H;  $\text{C}_5\text{Me}_4$ ), 2.11 (s, 6H;  $\text{C}_5\text{Me}_4$ ), 2.31 (s, 6H;  $\text{NMe}_2$ ), 3.24 (d,  $^3J(\text{H,H}) = 12.0 \text{ Hz}$ , 8H;  $\text{CH}_2\text{CHCH}_2$ ), 6.48–6.56 (m, 2H;  $\text{CH}_2\text{CHCH}_2$ ), 6.86 (d,  $^3J(\text{H,H}) = 12.0 \text{ Hz}$ , 1H;  $o\text{-NC}_6\text{H}_4$ ), 7.04 (t,  $^3J(\text{H,H}) = 12.0 \text{ Hz}$ , 1H;  $p\text{-NC}_6\text{H}_4$ ), 7.09 (t,  $^3J(\text{H,H}) = 12.0 \text{ Hz}$ , 1H;  $m\text{-NC}_6\text{H}_4$ ), 7.20 ppm (d,  $^3J(\text{H,H}) = 6.0 \text{ Hz}$ , 1H;  $m\text{-NC}_6\text{H}_4$ );  $^{13}\text{C NMR}$  (150 MHz,  $[\text{D}_6]$ benzene,  $25^\circ\text{C}$ ):  $\delta = 12.42$  (s, 2C;  $\text{C}_5\text{Me}_4$ ), 12.53 (s, 2C;  $\text{C}_5\text{Me}_4$ ), 50.88 (s, 2C;  $\text{NMe}_2$ ), 69.26 (s, 2C;  $\text{CH}_2\text{CHCH}_2$ ), 69.33 (s, 2C;  $\text{CH}_2\text{CHCH}_2$ ), 115.87 (s, 2C;  $\text{C}_5\text{Me}_4$ ), 117.32 (s, 2C;  $\text{C}_5\text{Me}_4$ ), 120.86 (s, 1C;  $o\text{-NC}_6\text{H}_4$ ), 121.45 (s, 1C; *ipso*- $\text{C}_5\text{Me}_4$ ), 127.36 (s, 1C;  $p\text{-NC}_6\text{H}_4$ ), 128.79 (s, 1C;  $m\text{-NC}_6\text{H}_4$ ), 133.96 (s, 1C;  $o\text{-C}_5\text{Me}_4\text{C}_6\text{H}_4$ ), 135.39 (s, 1C; *ipso*- $\text{C}_5\text{Me}_4\text{C}_6\text{H}_4$ ), 151.17 (s, 2C;  $\text{CH}_2\text{CHCH}_2$ ), 157.00 ppm (s, 1C; *ipso*- $\text{NC}_6\text{H}_4$ ); elemental analysis calcd (%) for  $\text{C}_{23}\text{H}_{32}\text{NLu}$ : C 55.53, H 6.48, N 2.82; found: C 56.02, H 6.51, N 2.71.

**Synthesis of complex 3a:** To a suspension of  $\text{YCl}_3$  (0.195 g, 1.0 mmol) in THF (20 mL) was added 1 equiv of  $(\text{C}_5\text{Me}_4\text{-C}_5\text{H}_4\text{N})\text{Li}$  (0.206 g, 1.0 mmol), which was prepared by the reaction of  $\text{C}_5\text{Me}_4\text{H-C}_5\text{H}_4\text{N}$  with *n*BuLi, slowly at RT under a nitrogen atmosphere. The mixture was stirred for 4 h to afford a clear solution, to which  $\text{C}_3\text{H}_5\text{MgCl}$  (1.0 mL,

2.0 mmol, 2.0 M in THF) was added. The resulting dark-red solution was left overnight. Removal of volatile compounds yielded a dark-red residue, which was extracted with toluene. Evaporation of the solvent afforded compound **3a** as an orange–yellow crystalline solid (0.218 g, 58.2%). Recrystallization from toluene and *n*-hexane gave yellow single crystals suitable for X-ray analysis.  $^1\text{H NMR}$  (400 MHz,  $[\text{D}_6]$ benzene,  $25^\circ\text{C}$ ):  $\delta = 1.89$  (s, 6H;  $\text{C}_5\text{Me}_4$ ), 2.17 (s, 6H;  $\text{C}_5\text{Me}_4$ ), 2.94 (d,  $^3J(\text{H,H}) = 15.0 \text{ Hz}$ , 4H; *anti*- $\text{CH}_2\text{CHCH}_2$ ), 3.21 (d,  $^3J(\text{H,H}) = 7.8 \text{ Hz}$ , 4H; *syn*- $\text{CH}_2\text{CHCH}_2$ ), 6.34–6.43 (quintet, 2H;  $\text{CH}_2\text{CHCH}_2$ ), 6.49–6.52 (m, 1H;  $\text{C}_5\text{H}_4\text{N}$ ), 7.00–7.06 (m, 2H;  $\text{C}_5\text{H}_4\text{N}$ ), 7.88 ppm (d,  $^3J(\text{H,H}) = 4.8 \text{ Hz}$ , 1H;  $\text{C}_5\text{H}_4\text{N}$ );  $^{13}\text{C NMR}$  (100 MHz,  $[\text{D}_6]$ benzene,  $25^\circ\text{C}$ ):  $\delta = 11.33$  (s, 2C;  $\text{C}_5\text{Me}_4$ ), 11.43 (s, 2C;  $\text{C}_5\text{Me}_4$ ), 69.56 (s, 4C;  $\text{CH}_2\text{CHCH}_2$ ), 108.07 (s, 1C;  $\text{C}_5\text{Me}_4$ ), 118.04 (s, 2C;  $\text{C}_5\text{Me}_4$ ), 118.41 (s, 2C;  $\text{C}_5\text{Me}_4$ ), 121.91 (s, 1C;  $\text{C}_5\text{H}_4\text{N}$ ), 125.78 (s, 1C;  $\text{C}_5\text{H}_4\text{N}$ ), 137.84 (s, 1C;  $\text{C}_5\text{H}_4\text{N}$ ), 147.90 (s, 2C;  $\text{CH}_2\text{CHCH}_2$ ), 150.01 (s, 1C;  $\text{C}_5\text{H}_4\text{N}$ ), 158.86 ppm (s, 1C; *ipso*- $\text{C}_5\text{H}_4\text{N}$ ); elemental analysis calcd (%) for  $\text{C}_{20}\text{H}_{26}\text{NY}$ : C 65.04, H 7.10, N 3.79; found: C 64.80, H 7.01, N 3.68.

**Synthesis of complex 3b:** To a suspension of  $\text{ScCl}_3$  (0.151 g, 1.0 mmol) in THF (20 mL) was slowly added 1 equiv of  $(\text{C}_5\text{Me}_4\text{-C}_5\text{H}_4\text{N})\text{Li}$  (0.206 g, 1.0 mmol), which was prepared by the reaction of ligand  $\text{C}_5\text{Me}_4\text{H-C}_5\text{H}_4\text{N}$  with *n*BuLi, at RT under a nitrogen atmosphere. The mixture was stirred for 4 h to afford a clear solution, before  $\text{C}_3\text{H}_5\text{MgCl}$  (1.0 mL, 2.0 mmol, 2.0 M in THF) was added. The resulting dark-red solution was left overnight. Removal of the volatile compounds yielded a dark-red residue, which was extracted with toluene. Evaporation of the solvent afforded compound **3b** as an orange–red crystalline solid (0.173 g, 52.3%). Recrystallization from toluene and *n*-hexane gave single crystals suitable for X-ray analysis.  $^1\text{H NMR}$  (400 MHz,  $[\text{D}_6]$ benzene,  $25^\circ\text{C}$ ):  $\delta = 1.84$  (s, 6H;  $\text{C}_5\text{Me}_4$ ), 2.11 (s, 6H;  $\text{C}_5\text{Me}_4$ ), 3.27 (d,  $^3J(\text{H,H}) = 12.4 \text{ Hz}$ , 8H;  $\text{CH}_2\text{CHCH}_2$ ), 6.10–6.16 (quintet, 2H;  $\text{CH}_2\text{CHCH}_2$ ), 6.48–6.51 (m, 1H;  $\text{C}_5\text{H}_4\text{N}$ ), 6.97–7.04 (m, 2H;  $\text{C}_5\text{H}_4\text{N}$ ), 7.93 ppm (d,  $^3J(\text{H,H}) = 5.2 \text{ Hz}$ , 1H;  $\text{C}_5\text{H}_4\text{N}$ );  $^{13}\text{C NMR}$  (100 MHz,  $[\text{D}_6]$ benzene,  $25^\circ\text{C}$ ):  $\delta = 12.13$  (s, 2C;  $\text{C}_5\text{Me}_4$ ), 12.52 (s, 2C;  $\text{C}_5\text{Me}_4$ ), 74.22 (s, 4C;  $\text{CH}_2\text{CHCH}_2$ ), 108.63 (s, 1C;  $\text{C}_5\text{Me}_4$ ), 119.82 (s, 2C;  $\text{C}_5\text{Me}_4$ ), 120.08 (s, 2C;  $\text{C}_5\text{Me}_4$ ), 122.35 (s, 1C;  $\text{C}_5\text{H}_4\text{N}$ ), 125.37 (s, 1C;  $\text{C}_5\text{H}_4\text{N}$ ), 138.12 (s, 1C;  $\text{C}_5\text{H}_4\text{N}$ ), 146.49 (s, 2C;  $\text{CH}_2\text{CHCH}_2$ ), 149.87 (s, 1C;  $\text{C}_5\text{H}_4\text{N}$ ), 158.67 ppm (s, 1C; *ipso*- $\text{C}_5\text{H}_4\text{N}$ ); elemental analysis calcd (%) for  $\text{C}_{20}\text{H}_{26}\text{NSc}$ : C 73.82, H 8.05, N 4.30; found: C 74.12, H 8.21, N 4.14.

**Synthesis of ligand  $\text{C}_{13}\text{H}_9\text{-C}_5\text{H}_4\text{N}$ :** *n*BuLi (30 mL, 2.50 mol L $^{-1}$ ) was added dropwise to a solution of fluorene (12.467 g, 75.0 mmol) in THF (50 mL) at  $-40^\circ\text{C}$ , and the mixture was slowly allowed to warm to RT and stirred overnight. A solution of 2-bromopyridine (11.850 g, 75.0 mmol) in THF was added dropwise to fluorenyllithium over 30 min at  $-40^\circ\text{C}$ . The mixture was slowly allowed to warm to RT and the reaction was stirred for a further 12 h. Removal of the volatile compounds in vacuo gave an oily residue, which was purified by column chromatography on silica gel (*n*-hexane/EtOAc, 3:1) to afford compound  $\text{C}_{13}\text{H}_9\text{-C}_5\text{H}_4\text{N}$  in 61.0% yield (11.131 g).  $^1\text{H NMR}$  (400 MHz,  $[\text{D}_6]$ benzene,  $25^\circ\text{C}$ ):  $\delta = 5.60$  (s, 1H; fluorene H), 6.53 (d,  $^3J(\text{H,H}) = 8.0 \text{ Hz}$ , 1H;  $\text{C}_5\text{H}_4\text{N}$ ), 6.64–6.67 (m, 1H;  $\text{C}_5\text{H}_4\text{N}$ ), 6.85–6.91 (m, 1H;  $\text{C}_5\text{H}_4\text{N}$ ), 7.18 (t,  $^3J(\text{H,H}) = 20.0 \text{ Hz}$ , 2H; *ArH*), 7.31 (t,  $^3J(\text{H,H}) = 20.0 \text{ Hz}$ , 2H; *ArH*), 7.54 (d,  $^3J(\text{H,H}) = 8.0 \text{ Hz}$ , 2H; *ArH*), 7.73 (d,  $^3J(\text{H,H}) = 8.0 \text{ Hz}$ , 2H; *ArH*), 8.64 ppm (d,  $^3J(\text{H,H}) = 4.0 \text{ Hz}$ , 1H;  $\text{C}_5\text{H}_4\text{N}$ );  $^{13}\text{C NMR}$  (100 MHz,  $[\text{D}_6]$ benzene,  $25^\circ\text{C}$ ):  $\delta = 57.61$  (s, 1C; fluorene C), 120.69, 121.64, 122.19, 126.36, 128.12, 136.79, 142.21, 147.39, 150.18 (s, 16C; *ArC* and  $\text{C}_5\text{H}_4\text{N}$ ), 162.63 ppm (s, 1C; *ipso*- $\text{C}_5\text{H}_4\text{N}$ ); elemental analysis calcd (%) for  $\text{C}_{18}\text{H}_{13}\text{N}$ : C 88.86, H 5.39, N 5.76; found: C 89.13, H 5.24, N 5.59.

**Synthesis of complex 4a:** To a solution of  $[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$  (0.495 g, 1.0 mmol) in toluene (10 mL) was slowly added a solution of 1 equiv of  $\text{C}_{13}\text{H}_9\text{-C}_5\text{H}_4\text{N}$  (0.243 g, 1.0 mmol) in toluene (10 mL) at RT under a nitrogen atmosphere. The mixture was stirred for 30 min to afford a clear red solution. Evaporation of the solvent gave compound **4a** as a red crystalline solid (0.314 g, 54.3%). Recrystallization from *n*-hexane and toluene gave single crystals suitable for X-ray analysis.  $^1\text{H NMR}$  (400 MHz,  $[\text{D}_6]$ benzene,  $25^\circ\text{C}$ ):  $\delta = -0.31$  (d,  $^2J(\text{Y,H}) = 4.0 \text{ Hz}$ , 4H;  $\text{YCH}_2\text{SiMe}_3$ ), 0.35 (s, 18H;  $\text{CH}_2\text{SiMe}_3$ ), 0.90 (br s, 4H; thf), 2.54 (br s, 4H; thf), 6.45 (t,  $^3J(\text{H,H}) = 12.0 \text{ Hz}$ , 1H;  $\text{C}_5\text{H}_4\text{N}$ ), 7.09–7.13 (m, 1H;  $\text{C}_5\text{H}_4\text{N}$ ), 7.26 (t,  $^3J(\text{H,H}) = 16.0 \text{ Hz}$ , 2H; *ArH*), 7.56–7.61 (m, 3H;  $\text{C}_5\text{H}_4\text{N}$  and *ArH*), 8.08 (d,



$^3J(\text{H,H})=8.0$  Hz, 2H; ArH), 8.12 (d,  $^3J(\text{H,H})=8.0$  Hz, 2H; ArH), 8.52 ppm (d,  $^3J(\text{H,H})=4.0$  Hz, 1H;  $\text{C}_5\text{H}_4\text{N}$ );  $^{13}\text{C}$  NMR (100 MHz,  $[\text{D}_6]\text{benzene}$ , 25°C):  $\delta=4.57$  (s, 6C;  $\text{CH}_2\text{SiMe}_3$ ), 25.05 (s, 2C; thf), 39.20 (d,  $J(\text{Y,C})=43.0$  Hz, 2C;  $\text{YCH}_2\text{SiMe}_3$ ), 70.38 (s, 2C; thf), 86.62 (s, 1C; fluorene C), 113.97, 117.39, 119.67, 121.12, 123.87, 127.54, 131.35, 136.70, 140.24, 147.64 (s, 16C; ArC and  $\text{C}_5\text{H}_4\text{N}$ ), 157.23 ppm (s, 1C; *ipso*- $\text{C}_5\text{H}_4\text{N}$ ); elemental analysis calcd (%) for  $\text{C}_{30}\text{H}_{42}\text{ONSi}_2\text{Y}$ : C 62.37, H 7.33, N 2.42; found: C 62.75, H 7.43, N 2.31.

**Synthesis of complex 4b:** To a solution of  $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$  (0.451 g, 1.0 mmol) in toluene (10 mL) was slowly added a solution of 1 equiv of  $\text{C}_{15}\text{H}_9\text{-C}_5\text{H}_4\text{N}$  (0.243 g, 1.0 mmol) in toluene (10 mL) at RT under a nitrogen atmosphere. The mixture was stirred for 30 min to afford a clear red solution. Evaporation of the solvent gave compound **4b** as a red crystalline solid (0.321 g, 60.1%). Recrystallization from *n*-hexane and toluene gave single crystals suitable for X-ray analysis.  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]\text{benzene}$ , 25°C):  $\delta=0.20$  (s, 4H;  $\text{ScCH}_2\text{SiMe}_3$ ), 0.34 (s, 18H;  $\text{CH}_2\text{SiMe}_3$ ), 0.90 (br s, 4H; thf), 2.55 (br s, 4H; thf), 6.47–6.50 (m, 1H;  $\text{C}_5\text{H}_4\text{N}$ ), 7.08–7.12 (m, 1H;  $\text{C}_5\text{H}_4\text{N}$ ), 7.30 (t,  $^3J(\text{H,H})=16.0$  Hz, 2H; ArH), 7.47 (d,  $^3J(\text{H,H})=8.0$  Hz, 1H;  $\text{C}_5\text{H}_4\text{N}$ ), 7.55 (t,  $^3J(\text{H,H})=16.0$  Hz, 2H; ArH), 8.02 (d,  $^3J(\text{H,H})=8.0$  Hz, 2H; ArH), 8.13 (t,  $^3J(\text{H,H})=8.0$  Hz, 2H; ArH), 8.60 ppm (d,  $^3J(\text{H,H})=4.0$  Hz, 1H;  $\text{C}_5\text{H}_4\text{N}$ );  $^{13}\text{C}$  NMR (100 MHz,  $[\text{D}_6]\text{benzene}$ , 25°C):  $\delta=4.14$  (s, 6C;  $\text{CH}_2\text{SiMe}_3$ ), 25.12 (br s, 2C; thf), 46.45 (br s, 2C;  $\text{ScCH}_2\text{SiMe}_3$ ), 71.58 (br s, 2C; thf), 85.75 (s, 1C; fluorene C), 114.58, 117.34, 120.27, 120.87, 123.61, 127.12, 132.53, 137.73, 140.45, 147.32 (s, 16C; ArC and  $\text{C}_5\text{H}_4\text{N}$ ), 157.05 ppm (s, 1C; *ipso*- $\text{C}_5\text{H}_4\text{N}$ ); elemental analysis calcd (%) for  $\text{C}_{30}\text{H}_{42}\text{ONSi}_2\text{Sc}$ : C 67.50, H 7.93, N 2.62; found: C 67.81, H 8.01, N 2.51.

**Synthesis of complex 4c:** To a solution of  $[\text{Lu}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$  (0.581 g, 1.0 mmol) in toluene (10 mL) was slowly added a solution of 1 equiv of  $\text{C}_{15}\text{H}_9\text{-C}_5\text{H}_4\text{N}$  (0.243 g, 1.0 mmol) in toluene (10 mL) at RT under a nitrogen atmosphere. The mixture was stirred for 30 min to afford a clear red solution. Evaporation of the solvent afforded compound **4c** as a red crystalline solid (0.440 g, 66.3%). Recrystallization from *n*-hexane and toluene gave single crystals suitable for X-ray analysis.  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]\text{benzene}$ , 25°C):  $\delta=-0.54$  (s, 4H;  $\text{LuCH}_2\text{SiMe}_3$ ), 0.33 (s, 18H;  $\text{CH}_2\text{SiMe}_3$ ), 0.85 (br s, 4H; thf), 2.47 (br s, 4H; thf), 6.42 (t,  $^3J(\text{H,H})=12.0$  Hz, 1H;  $\text{C}_5\text{H}_4\text{N}$ ), 7.02–7.06 (m, 1H;  $\text{C}_5\text{H}_4\text{N}$ ), 7.26 (t,  $^3J(\text{H,H})=16.0$  Hz, 2H; ArH), 7.50 (d,  $^3J(\text{H,H})=8.0$  Hz, 1H;  $\text{C}_5\text{H}_4\text{N}$ ), 7.59 (t,  $^3J(\text{H,H})=16.0$  Hz, 2H; ArH), 8.03 (d,  $^3J(\text{H,H})=8.0$  Hz, 2H; ArH), 8.12 (t,  $^3J(\text{H,H})=8.0$  Hz, 2H; ArH), 8.48 ppm (d,  $^3J(\text{H,H})=4.0$  Hz, 1H;  $\text{C}_5\text{H}_4\text{N}$ );  $^{13}\text{C}$  NMR (100 MHz,  $[\text{D}_6]\text{benzene}$ , 25°C):  $\delta=4.69$  (s, 6C;  $\text{CH}_2\text{SiMe}_3$ ), 25.04 (s, 2C; thf), 43.69 (s, 2C;  $\text{LuCH}_2\text{SiMe}_3$ ), 70.60 (s, 2C; thf), 85.42 (s, 1C; fluorene C), 113.74, 117.44, 119.73, 121.02, 123.71, 127.29, 131.55, 137.37, 140.53, 147.76 (s, 16C; ArC and  $\text{C}_5\text{H}_4\text{N}$ ), 157.38 ppm (s, 1C; *ipso*- $\text{C}_5\text{H}_4\text{N}$ ); elemental analysis calcd (%) for  $\text{C}_{30}\text{H}_{42}\text{ONSi}_2\text{Lu}$ : C 54.28, H 6.38, N 2.11; found: C 54.71, H 6.24, N 2.01.

**Synthesis of complex 5:** To a solution of  $[\text{Y}(\text{CH}_2\text{C}_6\text{H}_4\text{-}o\text{-NMe}_2)_3]$  (0.492 g, 1.0 mmol) in THF (10 mL) was slowly added a solution of 1 equiv of  $\text{C}_{15}\text{H}_9\text{-C}_5\text{H}_4\text{N}$  (0.243 g, 1.0 mmol) in THF (10 mL) at RT under a nitrogen atmosphere. The mixture was stirred for 1 h to afford a clear red solution. Evaporation of the solvent afforded compound **5** as a red crystalline solid (0.351 g, 58.6%). Recrystallization from toluene gave single crystals suitable for X-ray analysis that contained one toluene molecule per unit cell.  $^1\text{H}$  NMR (600 MHz,  $[\text{D}_6]\text{benzene}$ , 25°C):  $\delta=1.36$  (br s, 4H;  $\text{YCH}_2$ ), 1.90 (s, 12H;  $\text{NMe}_2$ ), 2.21 (s, 3H; Ph-Me), 6.38 (t,  $^3J(\text{H,H})=12.0$  Hz, 1H;  $\text{C}_5\text{H}_4\text{N}$ ), 6.82 (t,  $^3J(\text{H,H})=12.0$  Hz, 2H; ArH), 6.89 (d,  $^3J(\text{H,H})=12.0$  Hz, 2H; ArH), 6.99 (d,  $^3J(\text{H,H})=6.0$  Hz, 2H; ArH), 7.04–7.59 (m, 15H;  $\text{C}_5\text{H}_4\text{N}$  and ArH), 8.17 (d,  $^3J(\text{H,H})=6.0$  Hz, 1H; ArH), 8.38 ppm (d,  $^3J(\text{H,H})=6.0$  Hz, 2H;  $\text{C}_5\text{H}_4\text{N}$  and ArH);  $^{13}\text{C}$  NMR (150 MHz,  $[\text{D}_6]\text{benzene}$ , 25°C):  $\delta=21.86$  (s, 1C; PhMe), 45.00 (br s, 4C;  $\text{NMe}_2$ ), 46.16 (d,  $J(\text{Y,C})=24.0$  Hz, 2C;  $\text{YCH}_2$ ), 88.82 (s, 1C; fluorene C), 114.96, 119.47, 119.84, 121.40, 121.79, 126.14, 128.79, 129.01, 129.78, 129.86, 136.51, 138.34, 138.77, 141.95, 147.76 (s, 34C; ArC and  $\text{C}_5\text{H}_4\text{N}$ ), 158.13 ppm (s, 1C; *ipso*- $\text{C}_5\text{H}_4\text{N}$ ); elemental analysis calcd (%) for  $\text{C}_{46}\text{H}_{56}\text{N}_3\text{Y}$ : C 72.11, H 6.05, N 7.01; found: C 72.64, H 5.93, N 6.91.

**Typical procedure for styrene polymerization:** (Table 1, run 7) A solution of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (9.2 mg, 10  $\mu\text{mol}$ ) in toluene (2 mL) was added to a solution of complex **3b** (3.2 mg, 10  $\mu\text{mol}$ ) in toluene (1 mL) in a 25 mL

flask under a nitrogen atmosphere. The mixture was stirred at RT for a few minutes and then 0.52 g (5 mmol) of styrene was added under vigorous stirring. The magnetic stirring was ceased after 1 min. The flask was then removed from the glove box. MeOH (2 mL) was added to terminate the polymerization. The mixture was then poured into MeOH (100 mL) to precipitate the polymer. The white polymer was collected by filtration, and dried under vacuum at 40°C to a constant weight (0.52 g, 100%).

**Characterization of polystyrene:** The molecular weights ( $M_n$ ) and molecular-weight distributions ( $M_w/M_n$ ) of the polystyrene chains were measured by gel permeation chromatography (GPC) on a PL-GPC 220 type high-temperature chromatograph equipped with three PL-gel 10  $\mu\text{m}$  Mixed-B LS type columns at 150°C. Solvent: 1,2,4-trichlorobenzene (TCB) containing 0.05 w/v % 2,6-di-*tert*-butyl-*p*-cresol (BHT); flow rate: 1.0 mL min<sup>-1</sup>. The calibration was made by polystyrene standard Easi Cal PS-1 (PL Ltd).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for  $^1\text{H}$  NMR; 100 MHz for  $^{13}\text{C}$  NMR) spectrometer in  $[\text{D}_4]1,2$ -dichlorobenzene at 125°C. The melting temperature ( $T_m$ ) of polystyrene was measured by DSC analysis on a Q 100 DSC from TA Instruments under a nitrogen atmosphere at heating and cooling rates of 10°C min<sup>-1</sup> (temperature range: 0–300°C).

**Crystal data of compound 1a:**  $\text{C}_{42}\text{H}_{64}\text{N}_2\text{Si}_2\text{Y}_2$ ;  $M_r=830.95$ ; monoclinic; space group  $P2_1/n$ ;  $a=13.7448(9)$ ,  $b=10.7030(7)$ ,  $c=14.5972(10)$  Å;  $\beta=95.3430(10)^\circ$ ;  $V=2138.1(2)$  Å<sup>3</sup>;  $Z=2$ ;  $\rho_{\text{calcd}}=1.291$  g cm<sup>-3</sup>;  $\mu(\text{MoK}\alpha)=27.86$  cm<sup>-1</sup>; 11 670 reflections measured; 4 192 unique reflections; 3 410 reflections with  $I_o > 2\sigma(I_o)$ . Final  $R1=0.0311$ ,  $wR2=0.0809$  (all data).

**Crystal data of compound 2b:**  $\text{C}_{23}\text{H}_{32}\text{NLu}$ ;  $M_r=497.47$ ; monoclinic; space group  $P2_1/c$ ;  $a=8.7374(4)$ ,  $b=18.6251(9)$ ,  $c=12.8889(6)$  Å;  $\beta=98.4020(10)^\circ$ ;  $V=2074.96(17)$  Å<sup>3</sup>;  $Z=4$ ;  $\rho_{\text{calcd}}=1.592$  g cm<sup>-3</sup>;  $\mu(\text{MoK}\alpha)=47.62$  cm<sup>-1</sup>; 13 088 reflections measured; 4 075 unique reflections; 3 616 reflections with  $I_o > 2\sigma(I_o)$ . Final  $R1=0.0201$ ,  $wR2=0.0487$  (all data).

**Crystal data of compound 3a:**  $\text{C}_{20}\text{H}_{26}\text{NY}$ ;  $M_r=369.33$ ; monoclinic; space group  $P2_1/c$ ;  $a=8.5196(6)$ ,  $b=17.4851(11)$ ,  $c=12.6913(8)$  Å;  $\beta=100.9200(10)^\circ$ ;  $V=1856.3(2)$  Å<sup>3</sup>;  $Z=4$ ;  $\rho_{\text{calcd}}=1.321$  g cm<sup>-3</sup>;  $\mu(\text{MoK}\alpha)=31.39$  cm<sup>-1</sup>; 10 271 reflections measured; 3 639 unique reflections; 3 012 reflections with  $I_o > 2\sigma(I_o)$ . Final  $R1=0.0297$ ,  $wR2=0.0776$  (all data).

**Crystal data of compound 3b:**  $\text{C}_{20}\text{H}_{26}\text{NSc}$ ;  $M_r=325.38$ ; monoclinic; space group  $P2_1/c$ ;  $a=8.4756(7)$ ,  $b=17.4988(15)$ ,  $c=12.4289(11)$  Å;  $\beta=101.0140(10)^\circ$ ;  $V=1809.4(3)$  Å<sup>3</sup>;  $Z=4$ ;  $\rho_{\text{calcd}}=1.194$  g cm<sup>-3</sup>;  $\mu(\text{MoK}\alpha)=4.04$  cm<sup>-1</sup>; 9 290 reflections measured; 3 186 unique reflections; 2 441 reflections with  $I_o > 2\sigma(I_o)$ . Final  $R1=0.0531$ ,  $wR2=0.1424$  (all data).

**Crystal data of compound 4a:**  $\text{C}_{30}\text{H}_{42}\text{NOSi}_2\text{Y}$ ;  $M_r=577.74$ ; monoclinic; space group  $P2_1/c$ ;  $a=11.8276(12)$ ,  $b=16.9901(17)$ ,  $c=15.5957(15)$  Å;  $\beta=94.326(2)^\circ$ ;  $V=3125.1(5)$  Å<sup>3</sup>;  $Z=4$ ;  $\rho_{\text{calcd}}=1.228$  g cm<sup>-3</sup>;  $\mu(\text{MoK}\alpha)=19.64$  cm<sup>-1</sup>; 18 603 reflections measured, 6 131 unique reflections; 4 743 reflections with  $I_o > 2\sigma(I_o)$ . Final  $R1=0.0344$ ,  $wR2=0.0891$  (all data).

**Crystal data of compound 4b:**  $\text{C}_{30}\text{H}_{42}\text{NOSi}_2\text{Sc}$ ;  $M_r=533.79$ ; monoclinic; space group  $P2_1/c$ ;  $a=11.6092(8)$ ,  $b=16.8593(12)$ ,  $c=15.6083(11)$  Å;  $\beta=94.5270(10)^\circ$ ;  $V=3045.4(4)$  Å<sup>3</sup>;  $Z=4$ ;  $\rho_{\text{calcd}}=1.164$  g cm<sup>-3</sup>;  $\mu(\text{MoK}\alpha)=3.42$  cm<sup>-1</sup>; 17 922 reflections collected, 5 948 unique reflections; 4 550 reflections with  $I_o > 2\sigma(I_o)$ . Final  $R1=0.0449$ ,  $wR2=0.1215$  (all data).

**Crystal data of compound 4c:**  $\text{C}_{30}\text{H}_{42}\text{NOSi}_2\text{Lu}$ ;  $M_r=663.80$ ; monoclinic; space group  $P2_1/c$ ;  $a=11.7431(6)$ ,  $b=16.9409(9)$ ,  $c=15.6286(8)$  Å;  $\beta=94.4990(10)^\circ$ ;  $V=3099.6(3)$  Å<sup>3</sup>;  $Z=4$ ;  $\rho_{\text{calcd}}=1.422$  g cm<sup>-3</sup>;  $\mu(\text{MoK}\alpha)=32.83$  cm<sup>-1</sup>; 18 375 reflections collected, 6 098 unique reflections; 5 208 reflections with  $I_o > 2\sigma(I_o)$ . Final  $R1=0.0233$ ,  $wR2=0.0560$  (all data).

**Crystal data of compound 5 plus one toluene molecule:**  $\text{C}_{43}\text{H}_{54}\text{N}_3\text{Y}$ ;  $M_r=691.72$ ; monoclinic; space group  $P2_1/n$ ;  $a=16.758(9)$ ,  $b=11.398(6)$ ,  $c=18.680(9)$  Å;  $\beta=102.856(9)^\circ$ ;  $V=3479(3)$  Å<sup>3</sup>;  $Z=4$ ;  $\rho_{\text{calcd}}=1.321$  g cm<sup>-3</sup>;  $\mu(\text{MoK}\alpha)=17.11$  cm<sup>-1</sup>; 18 986 reflections collected; 6 122 unique reflections; 5 208 reflections with  $I_o > 2\sigma(I_o)$ . Final  $R1=0.0575$ ,  $wR2=0.1588$  (all data).

CCDC-743600 (**1a**), CCDC-818172 (**2b**), CCDC-762574 (**3a**), CCDC-818173 (**3b**), CCDC-818174 (**4a**), CCDC-818175 (**4b**), CCDC-818176 (**4c**), and CCDC-818177 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif)

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (project Nos. 20934006, 51073148, and 51021003) and by the Ministry of Science and Technology of China (projects Nos. 2009AA03Z501 and 2011DF50650).

- [1] a) F. T. Edelmann, *Coord. Chem. Rev.* **2011**, *255*, 1834; b) M. Zimmermann, R. Anwänder, *Chem. Rev.* **2010**, *110*, 6194; c) J. F. Carpentier, S. M. Guillaume, E. Kirillov, Y. Sarazin, *C. R. Chim.* **2010**, *13*, 608.
- [2] For selected reviews, see: a) P. M. Zeimentz, S. Arndt, B. R. Elvidge, J. Okuda, *Chem. Rev.* **2006**, *106*, 2404; b) Z. Hou, Y. Luo, X. Li, *J. Organomet. Chem.* **2006**, *691*, 3114; c) H. Li, T. J. Marks, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15295; d) S. Arndt, J. Okuda, *Adv. Synth. Catal.* **2005**, *347*, 339; e) S. Hong, T. J. Marks, *Acc. Chem. Res.* **2004**, *37*, 673; f) J. Okuda, *Dalton Trans.* **2003**, 2367; g) Z. Hou, Y. Wakatsuki, *Coord. Chem. Rev.* **2002**, *231*, 1; h) S. Arndt, J. Okuda, *Chem. Rev.* **2002**, *102*, 1953; i) H. Schumann, J. A. Meese-Marktscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865.
- [3] a) S. Arndt, B. R. Elvidge, P. M. Zeimentz, T. P. Spaniol, J. Okuda, *Organometallics* **2006**, *25*, 793; b) P. G. Hayes, W. E. Piers, M. Parvez, *Organometallics* **2005**, *24*, 1173; c) L. D. Henderson, G. D. MacInnis, W. E. Piers, M. Parvez, *Can. J. Chem.* **2004**, *82*, 162; d) P. G. Hayes, W. E. Piers, M. Parvez, *J. Am. Chem. Soc.* **2003**, *125*, 5622; e) P. G. Hayes, W. E. Piers, R. McDonald, *J. Am. Chem. Soc.* **2002**, *124*, 2132; f) S. Hajala, W. P. Schaefer, J. E. Bercaw, *J. Organomet. Chem.* **1997**, *532*, 45.
- [4] a) S. Ge, A. Meetsma, B. Hessen, *Organometallics* **2009**, *28*, 719; b) N. Meyer, P. W. Roesky, M. Bambera, A. Meetsma, B. Hessen, K. Saliu, J. Takats, *Organometallics* **2008**, *27*, 1501; c) S. Bambera, F. Perazzolo, S. J. Boot, T. J. J. Sciarone, A. Meetsma, B. Hessen, *Organometallics* **2008**, *27*, 704; d) C. T. Carver, M. J. Monreal, P. L. Diaconescu, *Organometallics* **2008**, *27*, 363; e) S. Bambera, A. Meetsma, B. Hessen, *Organometallics* **2006**, *25*, 3454; f) L. W. M. Lee, W. E. Piers, M. R. J. Elsegood, W. Clegg, M. Parvez, *Organometallics* **1999**, *18*, 2947.
- [5] a) D. J. H. Emslie, W. E. Piers, M. Parvez, *Dalton Trans.* **2003**, 2615; b) D. J. H. Emslie, W. E. Piers, M. Parvez, R. McDonald, *Organometallics* **2002**, *21*, 4226; c) D. J. H. Emslie, W. E. Piers, R. McDonald, *J. Chem. Soc. Dalton Trans.* **2002**, 293.
- [6] For examples, see: a) C. Döring, W. P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* **2010**, 2853; b) D. M. Lyubov, G. K. Fukin, A. V. Cherkasov, A. S. Shavyrin, A. A. Trifonov, L. Luconi, C. Bianchini, A. Meli, G. Giambastiani, *Organometallics* **2009**, *28*, 1227; c) D. M. Lyubov, C. Döring, G. K. Fukin, A. V. Cherkasov, A. S. Shavyrin, R. Kempe, A. A. Trifonov, *Organometallics* **2008**, *27*, 2905; d) T. K. Panda, C. G. Hrib, P. G. Jones, J. Jenter, P. W. Roesky, M. Tamm, *Eur. J. Inorg. Chem.* **2008**, 4270; e) A. Ravasio, C. Zampa, L. Boggioni, I. Tritto, J. Hitzbleck, J. Okuda, *Macromolecules* **2008**, *41*, 9565; f) L. Zhang, T. Suzuki, Y. Luo, M. Nishiura, Z. Hou, *Angew. Chem.* **2007**, *119*, 1941; *Angew. Chem. Int. Ed.* **2007**, *46*, 1909; g) X. Li, J. Baldamus, M. Nishiura, O. Tardif, Z. Hou, *Angew. Chem.* **2006**, *118*, 8364; *Angew. Chem. Int. Ed.* **2006**, *45*, 8184; h) L. Zhang, Y. Luo, Z. Hou, *J. Am. Chem. Soc.* **2005**, *127*, 14562; i) X. Li, J. Baldamus, Z. Hou, *Angew. Chem.* **2005**, *117*, 984; *Angew. Chem. Int. Ed.* **2005**, *44*, 962; j) C. S. Tredget, F. Bonnet, A. R. Cowley, P. Mountford, *Chem. Commun.* **2005**, 3301; k) X. Li, Z. Hou, *Macromolecules* **2005**, *38*, 6767; l) B. D. Ward, S. Bellemin-Laponnaz, L. H. Gade, *Angew. Chem.* **2005**, *117*, 1696; *Angew. Chem. Int. Ed.* **2005**, *44*, 1668; m) B. R. Elvidge, S. Arndt, P. M. Zeimentz, T. P. Spaniol, J. Okuda, *Inorg. Chem.* **2005**, *44*, 6777; n) Y. Luo, J. Baldamus, Z. Hou, *J. Am. Chem. Soc.* **2004**, *126*, 13910; o) S. Bambera, M. W. Bouwkamp, A. Meetsma, B. Hessen, *J. Am. Chem. Soc.* **2004**, *126*, 9182; p) S. Arndt, T. P. Spaniol, J. Okuda, *Angew. Chem.* **2003**, *115*, 5229; *Angew. Chem. Int. Ed.* **2003**, *42*, 5075; q) S. C. Lawrence, B. D. Ward, S. R. Dubberley, C. M. Kozak, P. Mountford, *Chem. Commun.* **2003**, 2880; r) S. Arndt, T. P. Spaniol, J. Okuda, *Chem. Commun.* **2002**, 896; s) S. Bambera, D. van Leusen, A. Meetsma, B. Hessen, J. H. Teuben, *Chem. Commun.* **2001**, 637.
- [7] a) F. Guo, M. Nishiura, H. Koshino, Z. Hou, *Macromolecules* **2011**, *44*, 2400; b) L. Wang, D. Cui, Z. Hou, W. Li, Y. Li, *Organometallics* **2011**, *30*, 760; c) M. Nishiura, T. Mashiko, Z. Hou, *Chem. Commun.* **2008**, 2019; d) W. Zhang, M. Nishiura, T. Mashiko, Z. Hou, *Chem. Eur. J.* **2008**, *14*, 2167; e) X. Li, M. Nishiura, K. Mori, T. Mashiko, Z. Hou, *Chem. Commun.* **2007**, 4137; f) F. Jaroschik, T. Shima, X. Li, K. Mori, L. Ricard, X. F. Le Goff, F. Nief, Z. Hou, *Organometallics* **2007**, *26*, 5654; g) S. Harder, *Organometallics* **2005**, *24*, 373; h) L. E. Manzer, *J. Am. Chem. Soc.* **1978**, *100*, 8068.
- [8] a) N. Yu, M. Nishiura, X. Li, Z. Xi, Z. Hou, *Chem. Asian J.* **2008**, *3*, 1406; b) L. F. Sánchez-Barba, D. L. Hughes, S. M. Humphrey, M. Bochmann, *Organometallics* **2005**, *24*, 3792.
- [9] a) A. Rodrigues, E. Kirillov, T. Roisnel, A. Razavi, B. Vuillemin, J. F. Carpentier, *Angew. Chem.* **2007**, *119*, 7378; *Angew. Chem. Int. Ed.* **2007**, *46*, 7240; b) R. E. White, T. P. Hanusa, B. E. Kucera, *J. Am. Chem. Soc.* **2006**, *128*, 9622; c) C. K. Simpson, R. E. White, C. N. Carlson, D. A. Wroblewski, C. J. Kuehl, T. A. Croce, I. M. Steele, B. L. Scott, V. G. Young, Jr., T. P. Hanusa, A. P. Sattelberger, K. D. John, *Organometallics* **2005**, *24*, 3685; d) T. J. Woodman, M. Schormann, L. Hughes, M. Bochmann, *Organometallics* **2004**, *23*, 2972; e) T. J. Woodman, M. Schormann, D. L. Hughes, M. Bochmann, *Organometallics* **2003**, *22*, 3028; f) T. J. Woodman, M. Schormann, M. Bochmann, *Organometallics* **2003**, *22*, 2938.
- [10] a) Z. Jian, D. Cui, Z. Hou, X. Li, *Chem. Commun.* **2010**, 46, 3022; b) D. Robert, E. Abinet, T. Spaniol, J. Okuda, *Chem. Eur. J.* **2009**, *15*, 11937; c) A. S. Rodrigues, E. Kirillov, C. W. Lehmann, T. Roisnel, B. Vuillemin, A. Razavi, J. F. Carpentier, *Chem. Eur. J.* **2007**, *13*, 5548; d) W. J. Evans, B. L. Davis, T. M. Champagne, J. W. Ziller, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 12678; e) W. J. Evans, J. M. Perotti, J. W. Ziller, *J. Am. Chem. Soc.* **2005**, *127*, 3894; f) E. Kirillov, C. W. Lehmann, A. Razavi, J. F. Carpentier, *J. Am. Chem. Soc.* **2004**, *126*, 12240; g) S. Maiwald, C. Sommer, G. Müller, R. Taube, *Macromol. Chem. Phys.* **2002**, *203*, 1029; h) S. Maiwald, H. Weißenborn, C. Sommer, G. Müller, R. Taube, *J. Organomet. Chem.* **2001**, *640*, 1; i) R. Taube, S. Maiwald, J. Sieler, *J. Organomet. Chem.* **2001**, *621*, 327; j) S. Maiwald, C. Sommer, G. Müller, R. Taube, *Macromol. Chem. Phys.* **2001**, *202*, 1446; k) S. Maiwald, H. Weißenborn, H. Windisch, C. Sommer, G. Müller, R. Taube, *Macromol. Chem. Phys.* **1997**, *198*, 3305.
- [11] a) N. Ishihara, M. Kuramoto, M. Uoi, *Macromolecules* **1988**, *21*, 3356; b) N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* **1986**, *19*, 2464.
- [12] a) M. Malanga, *Adv. Mater.* **2000**, *12*, 1869; b) N. Tomotsu, N. Ishihara, T. H. Newman, M. T. Malanga, *J. Mol. Catal. A* **1998**, *128*, 167.
- [13] a) J. Schellenberg, *Prog. Polym. Sci.* **2009**, *34*, 688; b) J. Schellenberg, H. J. Leder, *Adv. Polym. Technol.* **2006**, *25*, 141; c) J. Schellenberg, N. Tomotsu, *Prog. Polym. Sci.* **2002**, *27*, 1925; d) A. S. Rodrigues, E. Kirillov, J. F. Carpentier, *Coord. Chem. Rev.* **2008**, *252*, 2115; e) C. Averbuj, E. Tish, M. S. Eisen, *J. Am. Chem. Soc.* **1998**, *120*, 8640; f) J. Okuda, E. Masoud, *Macromol. Chem. Phys.* **1998**, *199*, 543.
- [14] a) X. Xu, Y. Cheng, J. Sun, *Chem. Eur. J.* **2009**, *15*, 846; b) X. Fang, X. Li, Z. Hou, J. Assoud, R. Zhao, *Organometallics* **2009**, *28*, 517.
- [15] F. Bonnet, C. D. C. Violante, P. Roussel, A. Mortreux, M. Visseaux, *Chem. Commun.* **2009**, 3380.
- [16] a) Z. Jian, S. Tang, D. Cui, *Chem. Eur. J.* **2010**, *16*, 14007; b) K. C. Hultsch, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228; c) L. Pan, K. Zhang, M. Nishiura, Z. Hou, *Macromolecules* **2010**, *43*, 9591.
- [17] X. Li, M. Nishiura, L. Hu, K. Mori, Z. Hou, *J. Am. Chem. Soc.* **2009**, *131*, 13870.
- [18] Y. Mu, W. E. Piers, D. C. MacQuarrie, M. J. Zaworotko, V. G. Young Jr., *Organometallics* **1996**, *15*, 2720.
- [19] a) E. Kirillov, L. Toupet, C. W. Lehmann, A. Razavi, J. F. Carpentier, *Organometallics* **2003**, *22*, 4467; b) E. Kirillov, L. Toupet, C. W. Lehmann, A. Razavi, S. Kahlal, J. Y. Saillard, J. F. Carpentier, *Organometallics* **2003**, *22*, 4038; c) S. Harder, M. Lutz, W. G. Straub, *Or-*

- ganometallics* **1997**, *16*, 107; d) M. Bochmann, S. J. Lancaster, M. B. Hursthouse, M. Mazid, *Organometallics* **1993**, *12*, 4718.
- [20] M. H. Lee, J. W. Hwang, Y. Kim, J. Kim, Y. Han, Y. Do, *Organometallics* **1999**, *18*, 5124.
- [21] W. J. Evans, T. S. Gummersheimer, T. J. Boyle, J. W. Ziller, *Organometallics* **1994**, *13*, 1281.
- [22] M. A. Schmid, H. G. Alt, W. Milius, *J. Organomet. Chem.* **1997**, *541*, 3.
- [23] a) M. Enders, G. Ludwig, H. Pritzkow, *Organometallics* **2001**, *20*, 827; b) U. Siemeling, V. Vorfeld, B. Neumann, H. G. Stammler, *Chem. Ber.* **1995**, *128*, 481.
- [24] M. F. Lappert, R. Pearce, *J. Chem. Soc. Chem. Commun.* **1973**, 126.
- [25] a) E. B. Tjaden, D. C. Swenson, R. F. Jordan, *Organometallics* **1995**, *14*, 371; b) J. C. W. Chien, W. M. Tsai, M. D. Rausch, *J. Am. Chem. Soc.* **1991**, *113*, 8570.
- [26] Bruker, SMART version 5.054.
- [27] SAINT and SADABS, version 6.22, Bruker AXS Inc., Madison, WI (USA), **2000**.
- [28] G. M. Sheldrick, SHELXTL NT version 6.12, Bruker AXS Inc., Madison, WI (USA), **2000**.

Received: August 28, 2011

Revised: November 23, 2011

Published online: January 26, 2012