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

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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- and Fluorate (Flu) ligands were facile-functionalized cyclopentadienyl (Cp) hydrocarbyl complexes bearing N-type.

The past two decades have witnessed tremendous growth in polymerization catalysis. The number of reported rare-earth-metal–hydrocarbyl complexes, [Ln(C5Me4-C5H4N)Ln(C13H8-C5H4N)Ln]3 (Ln = Y (3a), Sc (3b)), which also contained electron-withdrawing pyridyl-Cp ligands, were also obtained selectively. Deprotonation of the bulky pyridyl-Flu ligand (C13H8-C5H4N) by [Ln(CH2SiMe3)3(thf)] generated the rare-earth-metal–dialkyl complexes, [Ln(C13H8-C5H4N)Ln(CH2SiMe3)3(thf)]. In which an unusual asymmetric η3-allyl bonding mode of Flu moiety was observed. Switching to the bidentate yttrium-trisallyl complex [Y(CH2C6H4-o-NEt2)Lu(η3-CH2C6H4-o-NEt2)] the same reaction conditions afforded the corresponding yttrium bis(aminobenzyl) complex [η3-C13H8-C5H4N)Ln(CH2C6H4-o-NEt2)]3 (5).

Keywords: cyclopentadienyl ligands • hydrocarbyl complexes • ligand effects • polymerization • rare-earth metals and other related catalytic transformations, such as olefin hydroisilylation and hydroamination.[3] The hydrocarbyl complexes that contain linked- or unlinked monocyclopenta-dienyl (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.[16, 18] In general, the rare-earth-metal–hydrocarbyl complexes reported to date contain a(η3)-alkyl and π-η3-
alloy groups. In the cases of those containing a(η3)-alkyl groups, such as CH3,[19] CH2-Ph,[18] CH2SiMe3-Ph,[18] and the extensively used CH3SiMe3,[16, 18] Lewis basic ligands, such as Et2O, 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 basic coordination hampers the access of olefin monomers to the active metal sites and severely decreases its activity. Recently, ortho-N,N-dimethylaminobenzyl (CH3-C5H4-NMe2-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...
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.\[7\] Meanwhile, to stabilize the stability and reactivity, π-η-allyl ligands, such as CH₂C(Me)=CH₂,\[10\] CH(SiMe₃)CH=CH(SiMe₃),\[9\] and the often-used CH₂CH=CH₂,\[10\] have been employed to prepare solvent-free rare-earth-metal-allyl complexes that offer higher stabilities and appropriate activities.

On the other hand, syndiastic polystyrene (sPS), first prepared by Ishihara et al. using a Cp-based titanium catalyst,\[11\] is a promising thermoplastic that has potential applications in engineering plastics because of its high melting point, high tensile modulus, and excellent physical properties.\[12\] Hitherto, a large number of titanium analogues of the general formula [CpTiX₃] (Cp = substituted Cp, X = halogen or alkoxy), [IndTiX₃] (Ind = indenyl), or [FluTiX₃] (Flu = fluorenyl) have been reported that exhibit obvious improvements in both catalytic activity and syndioselectivity for styrene polymerization.\[13\] 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-CMe₂-Cp-based lanthanide-alkyl or -aminobenzyl complexes,\[10n,m,f,14\] Ln-π-allyl complexes,\[10n,15] or Ln-BH₄ complexes\[15] 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.\[16\] In particular, studies on the structure–catalytic performance relationships remain scarce.\[10n,14a\]

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 toward the polymerization of styrene, among which the catalyst based on the (pyridyl-Cp)–scandium–bis(allyl) precursor exhibited notable activity and perfect syndioselectivity (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 syndioselectivity, 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\[17\] the simple alkyl-abstraction method, which involved the treatment of [Ln(CH₂SiMe₃)₃(thf)] with 1 equivalent of electron-donating aminophenyl–Cp ligand C₆H₄CH₂(CH₂SiMe₃)₃ at room temperature, afforded the binuclear monoalkyl complexes [(C₆H₄CH₂-α-NMe₂(μ-CH₂)₃)Ln(CH₂SiMe₃)₃](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 NMe₂ was confirmed by the presence of two doublet resonances (δ ≈ 1.52 and 1.93 ppm) in the ¹H NMR spectrum of compound 1a, which were assigned to the newly formed NCH₂ groups; these resonances were correlated to those at δ = 1.44 ppm and δ = 1.54 ppm in compound 1b.\[19\] The analogous C–H activation of NMe₂ has been observed previously when the reaction of a multitandate Cp’ ligand with ScCl₃ and LiCH₂SiMe₃ was performed at high temperature (70°C) over 6 days.\[18\] Thus, to confirm whether the reaction temperature prompted the C–H activation of the NMe₂ group in our case, the acid-base reaction was performed at 0 or −20°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 NMe₂ group in this CGC ligand was unavoidable. X-ray analysis revealed that complex 1a had a dimeric structure, with C₂ 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 Å; this planarity was in striking contrast to the heavily crooked six-membered ring in compound 1b.\[20\] Moreover, the C₆H₄Y–Y bond angle (96.7(3)°) in compound 1a was slightly larger than in the corresponding [(C₆H₄CH₂-α-NMe₂)Y(η¹-C₆H₄)](95.4(3)°),\[16a\] Similarly, the C₆H₄Sc₁–N₁ bond angle in compound 1b was as large as 101.5°. Not unexpectedly, there was a marked difference in the Y₁–N₁ bond lengths in compounds 1a and [(C₆H₄CH₂-α-NMe₂)Y(η¹-C₆H₄)](2.389(2) and 2.630(2) Å, respectively), which was a consequence of metal-
ation of the NMe₂ group by drawing the N amino atom into closer proximity to the yttrium center in compound 1a.

**Preparation of complex 2b**: Treatment of the electron-donating alkaline ligand salt (C₅Me₄-C₆H₄-o-NMe₂)Li with LuCl₃ at room temperature for 4 h, followed by the in situ reaction with C₃H₅MgCl for another 12 h, afforded the target lutetium–bis(allyl) complex \[(C₅Me₄-C₆H₄-o-NMe₂)Lu(\text{allyl})_2\] in 58% yield (Scheme 2). The allyl group in compound 2b gave resonances at δ = 6.48–6.56 ppm and δ = 3.24 ppm, which were assigned to the methine and methylene protons, respectively. In this process, the C–H activation of NMe₂ group was not observed. The molecular structure of complex 2b was further confirmed by X-ray analysis. The ligand chelated to the Lu III center in a typical h⁵/k₁-CGC mode, whilst both of the allyl groups coordinated to the Lu III center in classical p-h₃ modes (Figure 2). The bond lengths between the Lu III center and the terminal allyl carbons (Lu1–C AT; average 2.579(3) Å) was comparable to that between the Lu III center and the central allyl carbons (Lu1–C AC; average 2.582(3) Å), consistent with the p-\(\eta^3\) binding mode. The C_pcent1-Lu1-N1 bite angle in compound 2b (96.7(3)°) was remarkably larger than in the pyridyl-Cp-attached lutetium–allyl complex \[(C₅Me₄-C₅H₄N)Lu(\text{allyl})_2\] (84.1(3)°)[16a] thus suggesting a more-crowded environment around the central metal arising from this aminophenyl-Cp CGC ligand. The crowded environment of complex 2b may impede its reactivity (see below).

**Preparation of complexes 3a and 3b**: The one-pot reaction of the electron-withdrawing alkaline ligand salt (C₅Me₄-C₅H₄N)Li with 1 equivalent of LnCl₃, followed by addition of 2 equivalents of C₃H₅MgCl in THF at room temperature afforded the corresponding rare-earth-metal–bis(allyl) complexes \[(C₅Me₄-C₅H₄N)Ln(\text{allyl})_2\] (Lₙ = Y (3a), 58%; Sc (3b), 52%; Scheme 3). Alternatively, the target products could be also obtained by the protonolysis of \[Ln(\text{allyl})_3(1,4-dioxane)\] and the addition of the electron-withdrawing pyridyl-Cp compound, C₅Me₄H-C₅H₄N, in THF.[16a] X-ray diffraction analysis revealed that the pyridyl-Cp ligand coordinated to the central metal atom in an \(\eta^1/\eta^1\) fashion, thereby generating a CGC-geometry, whilst the two allyl moieties coordinated to the central metal atom in \(\eta^1\) modes with one allyl group prone and the other supine in the solid state (Figure 3 and Figure 4). The \(^1H\) NMR spectrum of yttrium complex 3a showed that the central allylic group
protons (methine) gave 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 $[(\text{C}_5\text{Me}_5)\text{SiMe}_3]\text{Sc}(\eta^3-\text{C}_4\text{H}_4\text{SiMe}_3)\text{Cl}]$.[8a] The bond lengths between the Y III atom and the terminal allyl carbons in compound 3a (Y–CAT; average 2.600(3) Å) were shorter than those between the Y III atom and the central allyl carbon atoms (Y–C AC; average 2.617(3) Å). In contrast, the average bond length between the Sc III center and the terminal carbon atoms of the allyl groups (Sc1–C AT; average 2.483(4) Å) was comparable to that between the Sc III atom and the central carbon atoms of the allyl groups (Sc1–C AC; average 2.476(4) Å); both distances were slightly longer than the corresponding distances in $[(\text{C}_5\text{Me}_5)\text{SiMe}_3]\text{Sc}(\eta^3-\text{C}_4\text{H}_4)\text{Cl}]$ (Sc–C AT: 2.445(5) Å; Sc–C AC: 2.441(6) Å).[8a] The bond lengths between the Y III atom and the central allylic carbon atoms (Y–C AC; average 2.617(3) Å) were shorter than those between the Y III atom and the terminal carbon atoms of the allyl groups (Sc1–C AT; average 2.483(4) Å) in complex 3b. This open environment was also demonstrated by the Y–C cent distances: 3a (2.370(2)) > 2a (2.349(2)) > 1a (2.347(2)). Similarly, the bond lengths between the Sc III center and the terminal carbon atoms of the allyl groups (Sc1–C AT; average 2.483(4) Å) were much smaller than in complex 2a (95.4(3)°), thus suggesting a more-open environment around the Y III ion in complex 3a. This open environment 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$_3$H$_7$-C$_5$H$_4$N, a more-bulky ligand, was designed and prepared by the treatment of fluorene with butyllithium at $-40^\circ$C and subsequent reaction with 2-bromopyridine at room temperature (Scheme 4). The $^1$H NMR spectrum of 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(\text{CH}_2\text{SiMe}_3)_2(\text{thf})]$_3$ in toluene selectively generated alkyl complexes 4a–4c (Scheme 5). The $^1$H NMR
lengths and angles 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).

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).

The acid-base reaction between the yttrium-tris(aminobenzyl) compound [Y(CH3C6H5-o-NMe2)] and 1 equivalent of C13H9-C5H4N in THF at room temperature afforded the corresponding yttrium-bis(aminobenzyl) complex 5 in 59% yield (Scheme 6). NMR spectroscopic analysis of compound 5 revealed that the methylene protons of the metal-aminobenzyl Y-CH2C6H4-NMe2 moieties gave a broad singlet at δ = 1.36 ppm. 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 η1-allyl/η1-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.
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 (ipsos and ortho) of the benzyl groups (Y1–C20, 2.89(5) Å; Y1–C25, 2.85(5) Å; Y1–C29, 2.77(5) Å; Y1–C34, 2.80(5) Å) were observed in compound 5. Such interactions have been observed in cationic aminobenzyl scandium complexes\(^{[7a,c]}\) but were absent in PNP-based yttrium–bis(aminobenzyl) complexes, where the bond lengths of the Y–C (ipsos and ortho phenyl carbon atoms) were in the range 3.137–3.328 Å.\(^{[b]}\) 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).\(^{[b]}\)

**Styrene polymerization:** It has been reported that lanthanide–hydrocarbyl complexes containing Ln-α–C or Ln-π–C bonds with appropriate ancillary ligands displayed good activity for styrene polymerization to provide 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 [Ph₃C][B(C₆F₅)₄], the electron-donating aminophenyl-Cp–yttrium–allyl complex (1a) did not show any activity towards styrene polymerization, either in the presence or absence of 10 equivalents of AlBu₃ (Table 1, runs 1 and 2, respectively). Under the same conditions, the electron-donating aminophenyl-Cp–yttrium/lanthanum 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 aminophenyl-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 [Ph₃C][B(C₆F₅)₄], 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

### Table 1. Polymerization of styrene (St) catalyzed by complexes 1a, 1b, 2a, 2b, 3a–3c, 4a–4c, and 5.\(^{[1]}\)

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<th>[S]/[Ln]</th>
<th>t [min]</th>
<th>Conv. [%]</th>
<th>Activity[a]</th>
<th>sPS[b] [%]</th>
<th>Mₙ[c] (× 10⁴)</th>
<th>Mₙ/Mₚ[d]</th>
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[a] Polymerization conditions: [La] (10 μmol), [Ph₃C][B(C₆F₅)₄] (10 μmol), AlBu₃ (100 μmol), toluene/monomer = 5 : 1 (v/v), Tₚ = 20°C, unless otherwise noted.
[b] Given in kgmol⁻¹h⁻¹. [c] Measured by ¹H and ¹³C NMR spectroscopy in [D₆] 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] [PhNMMe₃][B(C₆F₅)₄] (10 μmol). [h] Ref. [16a].
excellent activity (3.12 × 10^3 kg mol^−1 h^−1) for the polymerization of styrene, affording perfect sPS (rrrr > 99%) with high molecular weight and narrow molecular-weight distribution (Mw/Mn = 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 × 10^3 kg mol^−1 h^−1, which was comparable to the most-scandium systems reported so far.° The resultant PS remained purely syndiotactic (Table 1, run 8), as confirmed by the strong sharp singlets at δ = 145.67 ppm (ipso-Ph), 45.04 ppm (methylene), and δ = 41.67 ppm (methylene) in the 13C NMR spectrum, and by the strong endothermic peak at 271°C in the DSC curve (see the Supporting Information). Surprisingly, in the presence of [PhNMMe2H][B(C6F5)4] instead of [Ph3C][B(C6F5)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.°°

Intrigued by these notable results for complexes 3a–3c, which had η3-coordination modes of the Cp moieties, the catalysis of pyridyl-functionalized Flu–alkyl complexes 4a–4c, which contained asymmetric η3-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 [Ph3C][B(C6F5)4], the THF-solvated precursors 4a–4c, which contained asymmetric η3-allyl bonding modes, could not initiate the polymerization of styrene, even though they possessed the more active Ln-o-CH2SiMe3 bond. By adding 10 equivalents of AlBu3 to the above catalytic system, styrene was successfully polymerized in a much-lower activity to afford syndiotactic-enriched PS (rrrr = 81–85%; Table 1, runs 12–14). Similarly, in the presence of 1 equivalent of [Ph3C][B(C6F5)4] and 10 equivalents of AlBu3, solvent-free complex 5, which contained an asymmetric η3-allyl bonding mode, also only showed low activity for the polymerization of styrene to give syndiotactic-enriched PS (rrrr = 76%; Table 1, run 15). These results revealed that, in view of both activity and selectivity, an η3-π-coordination mode of the ancillary ligand was superior to an asymmetric η3-allyl bonding mode for styrene polymerization.°° This superiority may be because the asymmetric η3-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 [Ln(CH3SiMe3)][(thf)3] 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 facilely obtained by the one-pot metathetical reactions of LnCl, with lithium salts of the ligands and CxH2MgCl. The acid-base reaction between [Ln(CH3SiMe3)][(thf)3] or [Y(CH2C6H4-o-NMe2)3] and the bulky pyridyl-modified fluorene ligand straightforwardly yielded the corresponding rare-earth-metal–bis(allyl) or yttrium–bis(aminobenzyl) complexes with an unusual asymmetric η3-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, are conducive for the polymerization of bulky styrene.

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. 1H and 13CNMR 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 CaH2, stirring for 48 h and distilled under reduced pressure before use. C6H5MgCl (2.0m in THF) was purchased from Aldrich. The ligands C6Me6H-C6H4-o-NMe2 and C6Me6H-C6H4N were prepared according to literature procedures.°°° Complexes [Ln(CH3SiMe3)][(thf)3] and [Y(CH2C6H4-o-NMe2)3]°°° were synthesized as described previously. Organo-organoborates [Ph3C][B(C6F5)4] and [PhNMMe2][B(C6F5)4] were synthesized according to literature procedures.°°° 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°C on a Bruker SMART APEX difrac-
tometer with a CCD area detector, using graphite-monochromated MoKα radiation (λ = 0.71073 Å). Determination of the crystal class and unit cell parameters was carried out by the SMART program.230 The raw frame data were processed using SAINT and SADABS to yield the reflection data.230 The structures were solved using the SHELXS program.230 Refinement was performed on F² 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 [Y(CH₂SiMe₃)₂(thf)] (0.495 g, 1.0 mmol) in n-hexane (5 mL), 1 equiv of C₅Me₄CH₂OH-NMe₃ (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°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°C. ¹H NMR (400 MHz, [D₆]benzene, 25°C): δ = 1.15 (br s, 2H; YCH₂SiMe₃), −0.75 (brs 2H; YCH₂SiMe₃), 0.20 (m; 18H; CH₃SiMe₃), 1.52 (d; 3J(HH) = 12.2 Hz; 2H; NCH₂), 1.93 (d; 3J(HH) = 12.2 Hz; 2H; NCH₂), 2.05 (s; 6H; CMe₆), 2.07 (s; 6H; CMe₆), 2.25 (s; 6H; CMe₆), 2.41 (s; 6H; CMe₆), 2.67 (s; 6H; NMe₃), 7.09–7.29 ppm (m, 8H, NCH₃); ¹³C NMR (100 MHz, [D₆]benzene, 25°C): δ = 5.00 (3C; CMe₆), 5.34 (3C; CMe₆), 10.96, 11.91, 12.03, 12.29, 12.38, 12.73, 12.78, 12.83 (3C; CMe₆), 33.62, 34.08 (2C; YCH₂SiMe₃), 45.76, 45.87 (2C; CMe₆), 73.15 (3C; CMe₆), 119.47, 119.57, 121.74, 123.25, 123.64, 126.07, 127.30, 129.27, 133.32, 133.82, 134.47, 134.91, 151.39, 161.06 ppm (CH₃ and CMe₆); elemental analysis calcd (%) for C₅H₁₂N₃Si₂Y: 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, nBuLi (1.65 mL in n-hexane, 0.60 mL, 1.05 mmol) was added dropwise to a solution of C₅Me₄CH₂OH-NMe₃ (0.241 g, 1.0 mmol) in THF (15 mL) at −78°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 YCl₃ (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 LiCH₂SiMe₃ (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 LuCl₃ (0.281 g, 1.0 mmol) in THF (20 mL), 1 equiv of [C₅Me₄CH₂OH-NMe₃]Li (0.247 g, 1.0 mmol) in THF was slowly added 1 equiv of (C₅Me₄)₃C₄H₅ (1.0 mmol) in THF (15 mL). After reaction at −78°C for 30 min, the reaction was slowly warmed to RT and was left to react for another 12 h before being added to a suspension of YCl₃ (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 LiCH₂SiMe₃ (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 3b: To a suspension of Sc(C₂H₅O)₂ (0.151 g, 1.0 mmol) in THF (20 mL) was slowly added 1 equiv of [C₅Me₄CH₂OH-NMe₃]Li (0.206 g, 1.0 mmol), which was prepared by the reaction of C₅Me₄CH₂OH-NMe₃ with nBuLi, at RT under a nitrogen atmosphere. The mixture was stirred for 4 h to afford a clear solution, to which LiCH₂SiMe₃ (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 4c: To a solution of [Sc(SiH2)(C6H5)3] (0.541 g, 1.00 mmol) in toluene (10 mL) was slowly added a solution of 1 equiv of C6H5-HgCl2 (0.245 g, 1.00 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 complex 4c as a red crystalline solid (0.321 g, 60.1%). Recrystallization from n-hexane and toluene gave single crystals suitable for X-ray analysis. 1H NMR (400 MHz, D2-benzene, 25°C): δ = 0.30 (4H, 2CH2), 2.65 (4H, 2CH2), 5.25 (8H, 2ArH), 6.69 (4H, 2ArH), 6.71 (4H, 2ArH). 13C NMR (100 MHz, D2-benzene, 25°C): δ = 24.1 (2C; thf), 28.5 (2C; thf), 106.3 (4C; C6H5), 150.2 (2C; thf), 156.36 (1C). Selective 1H NMR resonances (J in Hz): 6.43 (m, 1H; C6H5), 7.28 (d, 2H; 1H C6H5), 7.30 (d, 2H; 1H C6H5), 7.44 (m, 1H; C6H5), 12.01 (s, 1H; OH). 31P NMR (80 MHz, CDCl3, 25°C): δ = 13.68 (1P, 31P). 13C NMR (100 MHz, CDCl3, 25°C): δ = 13.0 (1C, Si(CH3)3), 13.2 (1C, Si(CH3)3), 58.6 (4C, C6H5), 123.7 (2C, C6H5), 125.1 (4C, C6H5), 132.3 (2C, C6H5), 150.8 (1C, C6H5). 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 (Mn) and molecular-weight distributions (Mw/Mn) 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 µm 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. The calibration was made by polystyrene standard East Cal PS (PL Ltd). 1H and 13C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for 1H NMR; 100 MHz for 13C NMR) spectrometer in [D6]dichlorobenzene at 125°C. The melting temperature (Tm) 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⁻¹ (temperature range: 0–300°C).

Crystal data of compound 1a: C138H238N6Si2Y; M = 830.95; monochromic; space group P21/n; a = 13.7448(9), b = 10.7030(7), c = 14.5972(10) Å; β = 95.3430(10); V = 2138.12(12) Å³; Z = 2; ρcalcd = 1.291 g cm⁻³; ρMol = 27.86 cm⁻³; 11670 reflections measured; 4129 unique reflections; 3410 reflections with I > 2σ(I). Final R1 = 0.0311, wR2 = 0.0809 (all data).

Crystal data of compound 2b: C138H266N2Si2Y; M = 497.47; monochromic; space group P21/a; a = 8.7567(10), b = 18.6251(19), c = 13.8219(13) Å; β = 98.4028(10); V = 2074.96(17) Å³; Z = 4; ρcalcd = 1.592 g cm⁻³; ρMol = 47.62 cm⁻³; 13088 reflections measured; 4075 unique reflections; 3616 reflections with I > 2σ(I). Final R1 = 0.0201, wR2 = 0.0487 (all data).

Crystal data of compound 3a: C30H42NOSi2Y; M = 363.39; monochromic; space group P21/c; a = 8.5196(9), b = 17.4851(11), c = 12.6913(8) Å; β = 100.9200(10); V = 1856.32(12) Å³; Z = 4; ρcalcd = 1.321 g cm⁻³; ρMol = 31.39 cm⁻³; 10271 reflections measured; 3639 unique reflections; 3012 reflections with I > 2σ(I). Final R1 = 0.0297, wR2 = 0.0776 (all data).

Crystal data of compound 4b: C138H264N2Si2Y; M = 325.38; monochromic; space group P21/a; a = 8.6273(10), b = 18.6251(19), c = 12.6289(11) Å; β = 98.4028(10); V = 2074.96(17) Å³; Z = 4; ρcalcd = 1.592 g cm⁻³; ρMol = 47.62 cm⁻³; 13088 reflections measured; 4075 unique reflections; 3616 reflections with I > 2σ(I). Final R1 = 0.0201, wR2 = 0.0487 (all data).

Crystal data of compound 4a: C138H266NOSi2Y; M = 577.74; monochromic; space group P21/c; a = 11.8286(12), b = 16.9901(17), c = 15.5975(15) Å; β = 94.3226(2); V = 3125.15(3) Å³; Z = 4; ρcalcd = 1.228 g cm⁻³; ρMol = 19.64 cm⁻³; 18603 reflections measured, 6131 unique reflections, 4743 reflections with I > 2σ(I). Final R1 = 0.0344, wR2 = 0.0891 (all data).

Crystal data of compound 4c: C138H264NOSi2Y; M = 663.80; monochromic; space group P21/c; a = 11.7431(6), b = 16.9490(9), c = 15.6268(16) Å; β = 94.4990(10); V = 3096.06(3) Å³; Z = 4; ρcalcd = 1.422 g cm⁻³; ρMol = 32.83 cm⁻³; 18375 reflections collected, 5208 reflections with I > 2σ(I). Final R1 = 0.0233, wR2 = 0.0560 (all data).

Crystal data of compound 5 plus one toluene molecule: C138H264N6Y; M = 691.72; monochromic; space group P21/a; a = 16.7589(8), b = 11.3908(6), c = 18.6809(8) Å; β = 102.856(9°); V = 3479.1(3) Å³; Z = 4; ρcalcd = 1.321 g cm⁻³; ρMol = 17.11 cm⁻³; 18960 reflections collected; 6122 unique reflections; 5208 reflections with I > 2σ(I). Final R1 = 0.0575, wR2 = 0.1588 (all data).
[26] Bruker, SMART version 5.054.

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