

Half-sandwich rare-earth-metal derivatives bearing pyrrolidinyl-functionalized cyclopentadienyl ligand: synthesis, characterization and catalysis in syndiospecific polymerization of styrene†

Yunjie Luo,* Shuhui Chi and Jue Chen

Cite this: *New J. Chem.*, 2013, **37**, 2675

Received (in Montpellier, France)
26th February 2013,
Accepted 6th June 2013

DOI: 10.1039/c3nj00214d

www.rsc.org/njc

One-pot reaction of LnCl_3 with 1 equivalent of $\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8\text{Li}$ followed by addition of 2 equivalents of allylmagnesium chloride $\text{C}_3\text{H}_5\text{MgCl}$ or $\text{LiN}(\text{SiHMe}_2)_2$ in THF at room temperature afforded the half-sandwich rare-earth-metal bis(η^3 -allyl) complexes ($\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_2$ ($\text{Ln} = \text{Sc}$ (**1**), Y (**2**), Lu (**3**)) and the half-sandwich rare-earth-metal bis(silylamide) complexes ($\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8\text{Ln}[\text{N}(\text{SiHMe}_2)_2]_2$ ($\text{Ln} = \text{Sc}$ (**4**), Y (**5**), Lu (**6**)), respectively. All these complexes were well-characterized by elemental analysis, FT-IR spectroscopy, NMR spectroscopy and X-ray crystallography. The binary catalyst systems **1–3**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$] and the ternary catalyst systems **1–6**/[Ph_3C][$\text{B}(\text{C}_6\text{F}_5)_4$]/ Al^iBu_3 in toluene at room temperature showed activity toward the syndiospecific polymerization of styrene.

Introduction

Compared to rare-earth-metal metallocene complexes [$\text{Cp}_2\text{Ln-R}$] (Cp = monoanionic cyclopentadienyl ligand, Ln = rare-earth-metal, R = alkyl, hydrido, amide, *etc.*), half-sandwich rare-earth-metal complexes [CpLnR_2] have received intensive attention only in recent years owing to their unique performances in organic transformations and polymerizations.¹ However, the isolation and structural characterization of half-sandwich rare-earth-metal complexes usually is hampered for facile ligand scrambling in these complexes. To date, the most reported highly active half-sandwich rare-earth-metal complexes are rare-earth-metal hydrocarbyl complexes containing a $\sigma(\eta^1)$ -bond, such as CH_3 ,² CH_2Ph ,³ and CH_2SiMe_3 ,⁴ in which Lewis bases such as THF, Et_2O and DME are usually incorporated to stabilize the highly unsaturated Lewis acidic rare-earth-metal centers. However, the strong coordination of the Lewis base prevents the access of olefin monomers to the active metal site, and thus severely decreases the reactivity. From the viewpoint of the balance between stability and reactivity, introducing either a heteroatom side arm on the Cp ring to form so-called constrained geometry configuration (CGC) monoanionic ancillary ligand sets,⁵ or

adopting reactive hydrocarbyl groups such as multidentate chelating aminobenzyl group⁶ and $\pi(\eta^3)$ -allyl groups,⁷ proves to be the most efficient approach to prepare solvent-free, highly stable, and appropriately active rare-earth-metal complexes.

During our investigation into the structure–reactivity relationship of half-sandwich rare-earth-metal complexes, we became interested in exploiting thermo-stable, facilely accessible, and solvent-free rare-earth-metal bis(amide) complexes as appropriately active catalyst precursors.⁸ In this work, a new series of half-sandwich rare-earth-metal bis(silylamide) complexes bearing the pyrrolidinyl-functionalized cyclopentadienyl ligand were prepared and well-characterized. In order to compare the effects of active groups on catalytic polymerization, a class of rare-earth-metal bis(allyl) complexes with the same ancillary ligand was also prepared and characterized. These novel half-sandwich rare-earth-metal derivatives are thermally stable, solvent-free, and can serve as catalyst precursors in styrene polymerization. It was found that the effects of the central metals and the active groups on styrene polymerization were strikingly obvious, with the scandium complexes and the rare-earth-metal allyl complexes showing relatively higher activity. The polymerization afforded pure syndiotactic polystyrene with high syndiotacticity (*rrrr* > 99%). Here we report these results.

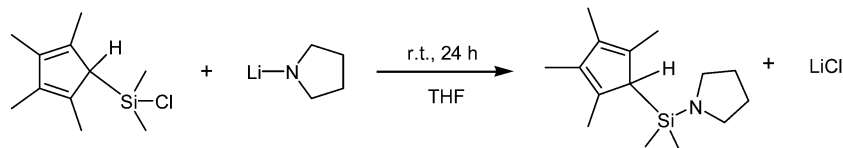
Results and discussion

The pyrrolidinyl-functionalized cyclopentadienyl ligand was synthesized by treatment of chloro-dimethyl-(2,3,4,5-tetramethyl-cyclopenta-2,4-dienyl)-silane ($\text{C}_5\text{Me}_4\text{HSiMe}_2\text{Cl}$) with 1 equivalent

Organometallic Chemistry Laboratory, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, People's Republic of China.

E-mail: hyj@nit.zju.edu.cn; Fax: +86-574-88130130; Tel: +86-574-88130085

† Electronic supplementary information (ESI) available: NMR spectra of **1–6**, and GPC curve, DSC curve and ^{13}C NMR spectrum of polymer samples. CCDC 917594–917599. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3nj00214d



Scheme 1 Preparation of the pyrrolidinyl-functionalized cyclopentadienyl ligand.

of pyrrolidinyl lithium C_4H_8NLi , which was prepared from the reaction of pyrrolidine C_4H_8NH with 1 equivalent of n -BuLi in THF at room temperature (Scheme 1). The ligand was obtained as a yellow oil in 95% isolated yield, and its formula was confirmed as $C_5Me_4HSiMe_2NC_4H_8$ by elemental analysis, GC-mass spectrometry, and NMR spectroscopy. Deprotonation of $C_5Me_4HSiMe_2NC_4H_8$ with one equimolar amount of $LiCH_2SiMe_3$ in diethyl ether at room temperature, after workup, quantitatively afforded $C_5Me_4SiMe_2NC_4H_8Li$ as a pale yellow powder.

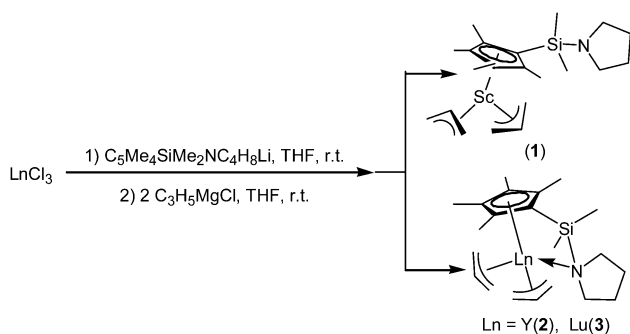
One-pot reaction of $LnCl_3$ with 1 equivalent of $C_5Me_4SiMe_2NC_4H_8Li$, followed by addition of 2 equivalents of allylmagnesium chloride C_3H_5MgCl in THF at room temperature afforded the half-sandwich rare-earth-metal bis(η^3 -allyl) complexes ($C_5Me_4SiMe_2NC_4H_8$) $Ln(\eta^3-C_3H_5)_2$ ($Ln = Sc$ (1), Y (2), Lu (3)) in 53–65% isolated yields (Scheme 2).

The similar reaction of $LnCl_3$ with $C_5Me_4SiMe_2NC_4H_8Li$ and $LiN(SiHMe_2)_2$ gave the half-sandwich rare-earth-metal bis-(silylamide) complexes ($C_5Me_4SiMe_2NC_4H_8$) $Ln[N(SiHMe_2)_2]_2$ ($Ln = Sc$ (4), Y (5), Lu (6)) in 51–62% isolated yields (Scheme 3).

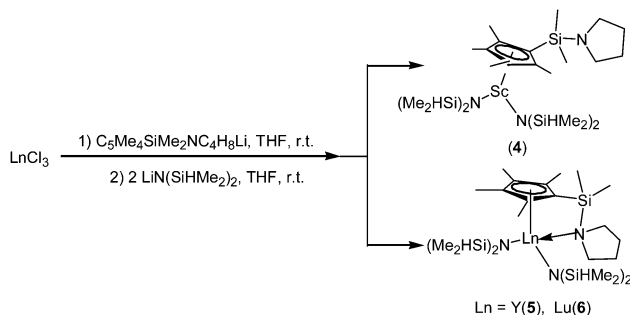
Elemental analysis, NMR spectroscopy, and X-ray crystallography confirmed the compositions of 1–6, and showed that they are neutral and mononuclear species. Notably, although 1–6 were prepared in THF, the incorporation of THF in these complexes was not observed. These complexes are thermally stable at ambient temperature in the glovebox, and show perfect solubility in THF, Et₂O, toluene, even in aliphatic solvents such as hexane and pentane.

The 1H NMR spectra of 1–6 in C_6D_6 at room temperature indicated that these complexes are fluxional in solution. In the cases of 1–3, 1H NMR spectra showed one sharp doublet signal at $\delta = 3.38$ (Sc), 3.00 (Y), 3.06 (Lu) for the terminal allylic protons and one multiplet at $\delta = 7.13$ (Sc), 6.33 (Y), 6.47 (Lu) for the central allylic protons. These results are consistent with those observed in $(C_5Me_4C_6H_4-o-NMe_2)Y(\eta^3-C_3H_5)_2$,^{5a} $(C_5Me_4C_5H_4N)-Sc(\eta^3-C_3H_5)_2$,^{4c} and in the unlinked-Cp-yttrium-allyl complex $(C_5Me_4SiMe_3)Y(\eta^3-C_3H_5)_2(THF)$.^{7a}

Single crystals of 1–6 suitable for X-ray diffraction were grown from hexane at -30 °C. The molecular structures are shown in Fig. 1–6, respectively. The crystallographic data are summarized in Table 1. In striking contrast to 2, 3, 5, and 6, in which the pyrrolidinyl-Cp ligand coordinates to the central metal in η^5/κ^1 CGC-geometric fashion, the pendant pyrrolidinyl moiety in 1 and 4 does not coordinate to the scandium center through the nitrogen atom. The η^5 -coordination mode of the pyrrolidinyl-Cp ligand in 1 and 4 may be the result of the small size of Sc^{3+} compared with Lu^{3+} and Y^{3+} .⁹ In 1, the two allyl moieties coordinate to the central metal in π - η^3 mode with one allyl group prone and the other supine (Fig. 1), whilst those in



Scheme 2 Synthesis of the half-sandwich rare-earth-metal bis(allyl) complexes 1–3.



Scheme 3 Synthesis of the half-sandwich rare-earth-metal bis(silylamide) complexes 4–6.

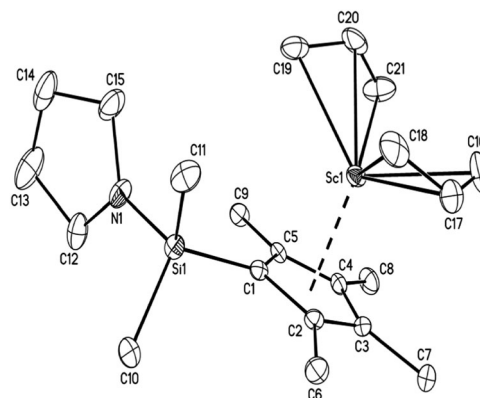


Fig. 1 Molecular structure of 1 with thermal ellipsoids at 10% probability. Selected bond distances (Å) and bond angles (°): Sc1–C1 = 2.451(5), Sc1–C2 = 2.461(5), Sc1–C3 = 2.482(5), Sc1–C4 = 2.464(5), Sc1–C5 = 2.453(5), Sc1–C16 = 2.418(8), Sc1–C17 = 2.431(7), Sc1–C18 = 2.395(7), Sc1–C19 = 2.438(7), Sc1–C20 = 2.414(7), Sc1–C21 = 2.428(8), $C_{p\text{centroid}}-Sc1 = 2.148(9)$, C17–Sc1–C20 = 112.6(3).

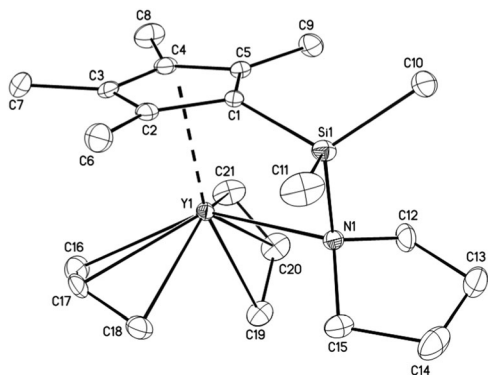


Fig. 2 Molecular structure of **2** with thermal ellipsoids at 30% probability. Selected bond distances (Å) and bond angles (°): Y1–C1 = 2.564(3), Y1–C2 = 2.684(3), Y1–C3 = 2.753(3), Y1–C4 = 2.684(3), Y1–C5 = 2.568(3), Y1–C16 = 2.625(3), Y1–C17 = 2.617(3), Y1–C18 = 2.600(3), Y1–C19 = 2.656(3), Y1–C20 = 2.637(3), Y1–C21 = 2.554(3), Cp_{centroid}–Y1 = 2.363(9), C17–Y1–C20 = 121.49(11), Cp_{centroid}–Y1–N1 = 94.1(3).

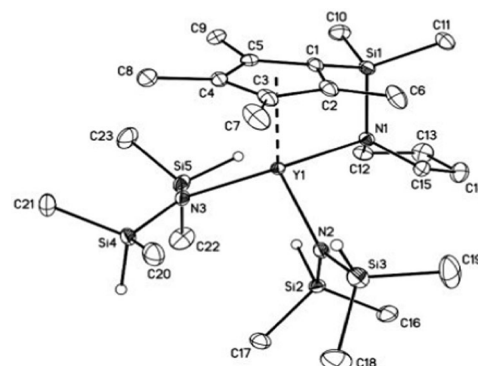


Fig. 5 Molecular structure of **5** with thermal ellipsoids at 20% probability. Selected bond distances (Å) and bond angles (°): Y1–C1 = 2.601(3), Y1–C2 = 2.657(3), Y1–C3 = 2.751(3), Y1–C4 = 2.750(3), Sc1–C5 = 2.656(3), Y1–N2 = 2.267(2), Y1–N3 = 2.275(3), Cp_{centroid}–Y1 = 2.397(8), N2–Y1–N3 = 99.93(9), Cp_{centroid}–Y1–N1 = 92.9(2).

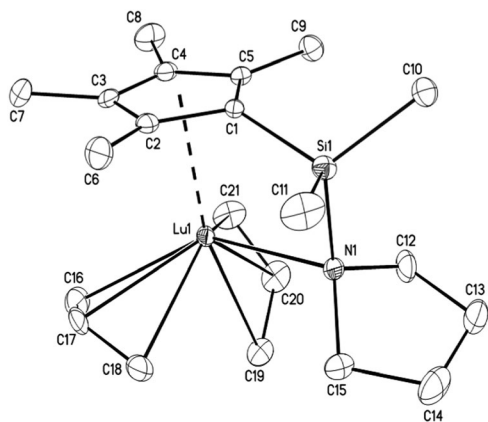


Fig. 3 Molecular structure of **3** with thermal ellipsoids at 30% probability. Selected bond distances (Å) and bond angles (°): Lu1–C1 = 2.523(4), Lu1–C2 = 2.637(4), Lu1–C3 = 2.728(4), Lu1–C4 = 2.647(4), Lu1–C5 = 2.528(4), Lu1–C16 = 2.596(4), Lu1–C17 = 2.564(4), Lu1–C18 = 2.539(5), Lu1–C19 = 2.633(4), Lu1–C20 = 2.592(4), Lu1–C21 = 2.506(4), Cp_{centroid}–Lu1 = 2.320(10), C17–Lu1–C20 = 120.69(16), Cp_{centroid}–Lu1–N1 = 95.9(3).

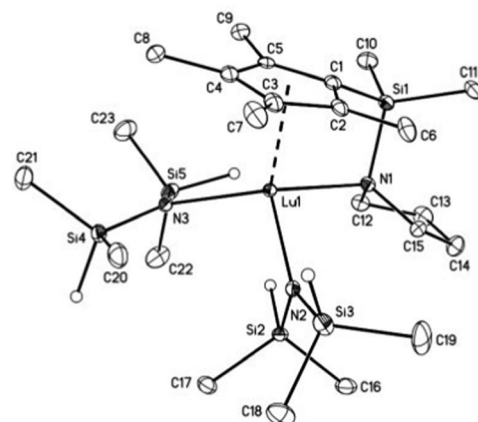


Fig. 6 Molecular structure of **6** with thermal ellipsoids at 20% probability. Selected bond distances (Å) and bond angles (°): Lu1–C1 = 2.550(4), Lu1–C2 = 2.612(4), Lu1–C3 = 2.708(4), Lu1–C4 = 2.707(4), Lu1–C5 = 2.618(4), Lu1–N2 = 2.216(3), Lu1–N3 = 2.237(3), Cp_{centroid}–Lu1 = 2.347(9), N2–Lu1–N3 = 99.30(11), Cp_{centroid}–Lu1–N1 = 94.5(3).

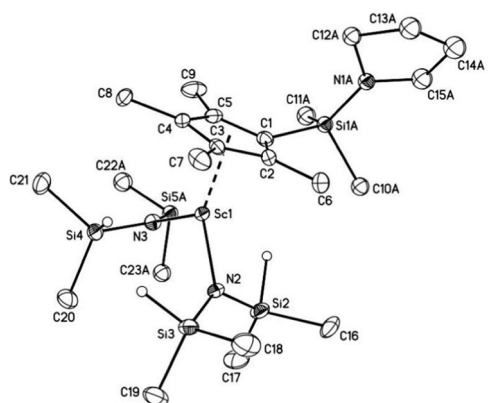


Fig. 4 Molecular structure of **4** with thermal ellipsoids at 10% probability. Selected bond distances (Å) and bond angles (°): Sc1–C1 = 2.437(4), Sc1–C2 = 2.464(4), Sc1–C3 = 2.488(4), Sc1–C4 = 2.504(4), Sc1–C5 = 2.473(4), Sc1–N2 = 2.086(3), Sc1–N3 = 2.073(4), Cp_{centroid}–Sc1 = 2.161(6), N2–Sc1–N3 = 109.57(15).

2 and **3** coordinate to the central metal atom in classic π - η^3 modes (Fig. 2 and Fig. 3). In **1–3**, the bond distances between the central metals and the terminal allyl carbons are comparable to those between the central metals and the central allyl carbons. The central metal Sc³⁺ in **4** is three-coordinated by one Cp ring in η^5 -fashion and two amide groups to form a trigonal geometry, if the Cp ring is regarded as occupying an independent vertex. This coordination mode is different to that in (C₅Me₅)Sc[N(SiHMe₂)₂]₂, in which the central metal Sc³⁺ is five-coordinated by one Cp ring in η^5 -fashion, two amide groups, and two agostic hydrogen atoms from Si–H to form a distorted trigonal bipyramidal geometry.^{8c} This difference may contribute to the steric hindrance of the pyrrolidinyl-Cp ligand. The Sc–N(SiHMe₂)₂ bond distances in **4** range from 2.073(4) to 2.086(3) Å, which are comparable with those in (C₅Me₅)Sc[N(SiHMe₂)₂]₂ (2.079(2) and 2.082(3) Å).^{8c} In the cases of **5** and **6**, however, the central metals are four-coordinated by one Cp ring in η^5/κ^1 mode and two amide groups to form a distorted tetrahedron geometry.

| | 1 | 2 | 3 | 4 | 5 | 6 |
|--|---|---|---|---|---|---|
| Chemical formula | C ₂₁ H ₃₆ NScSi | C ₂₁ H ₃₆ NSiY | C ₂₁ H ₃₆ LuNSi | C ₂₃ H ₅₄ N ₃ ScSi ₅ | C ₂₃ H ₅₄ N ₃ Si ₅ Y | C ₂₃ H ₅₄ LuN ₃ Si ₅ |
| Formula weight | 375.56 | 419.51 | 505.57 | 558.10 | 602.05 | 688.11 |
| Temperature (K) | 293(2) | 173(2) | 173(2) | 223(2) | 220(2) | 173(2) |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Triclinic | Monoclinic | Monoclinic |
| Space group | <i>P</i> 2 ₁ / <i>c</i> | <i>C</i> 2/ <i>c</i> | <i>C</i> 2/ <i>c</i> | <i>P</i> 1̄ | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ / <i>n</i> |
| <i>a</i> (Å) | 10.037(3) | 27.0591(11) | 26.9928(9) | 10.7456(16) | 9.9340(4) | 9.9233(3) |
| <i>b</i> (Å) | 16.030(4) | 9.9549(3) | 9.9102(2) | 10.7843(13) | 19.5918(7) | 19.4249(5) |
| <i>c</i> (Å) | 14.767(4) | 17.3059(7) | 17.1932(5) | 16.231(2) | 17.4660(13) | 17.3278(5) |
| α (°) | 90 | 90 | 90 | 108.818(6) | 90 | 90 |
| β (°) | 109.640(7) | 112.102(5) | 112.218(4) | 93.485(8) | 97.036(5) | 96.934(2) |
| γ (°) | 90 | 90 | 90 | 94.941(10) | 90 | 90 |
| Volume (Å ³) | 2237.8(10) | 4319.1(3) | 4257.8(2) | 1766.0(4) | 3373.7(3) | 3315.66(15) |
| <i>Z</i> | 4 | 8 | 8 | 2 | 4 | 4 |
| Reflec. collected | 16 621 | 10 594 | 11 010 | 14 209 | 15 282 | 15 664 |
| <i>R</i> _{int} | 0.1098 | 0.0304 | 0.0308 | 0.0277 | 0.0399 | 0.0369 |
| <i>R</i> ₁ , w <i>R</i> ₂ (all data) | <i>R</i> ₁ = 0.1675, w <i>R</i> ₂ = 0.2775 | <i>R</i> ₁ = 0.0515, w <i>R</i> ₂ = 0.0848 | <i>R</i> ₁ = 0.0376, w <i>R</i> ₂ = 0.0543 | <i>R</i> ₁ = 0.1150, w <i>R</i> ₂ = 0.2485 | <i>R</i> ₁ = 0.0684, w <i>R</i> ₂ = 0.0971 | <i>R</i> ₁ = 0.0403, w <i>R</i> ₂ = 0.0601 |

the presence of Al^iBu_3 , whereas it took 120 min to complete the polymerization in the absence of Al^iBu_3 (Table 2, runs 1 and 5). Although the polymerization activity was also significantly improved when Al^iBu_3 was introduced into the rare-earth-metal amide catalyst systems **4–6**/ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, the effect of the central metals on the polymerization was also obvious (Table 2, runs 7–9). In comparison, under the present conditions, the rare-earth-metal amide complexes showed lower activity than their allyl counterparts (Table 2, runs 5 and 7). The silylamide complexes gain catalytic activity upon activation with Al^iBu_3 , which may contribute to the formation of the rare-earth-metal alkyl complexes due to amide-alkyl exchange, as reported previously.^{8a,c,e}

Remarkably, the addition of excess Al^iBu_3 to the binary catalyst systems **1-6**/ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ to form the ternary catalyst systems **1-6**/ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Al}^i\text{Bu}_3$ dramatically increased the polymerization activity. For example, when employing **1** as the catalyst precursor at an initial feed ratio $[\text{M}]/[\text{Ln}] = 500$, the polymerization was completed in 20 min in

| Run | Complex | [Ln]:[B] ^b : [Al] | <i>t</i> (min) | Yield ^c (%) | sPS ^d (%) | <i>M</i> _n ^e × 10 ⁻⁴ | <i>M</i> _w / <i>M</i> _n ^e | <i>T</i> _m ^f (°C) |
|-----|---------------|------------------------------|----------------|------------------------|----------------------|---|--|---|
| 1 | 1 | 1:1:0 | 120 | > 99 | > 99 | 10.9 | 1.86 | 269 |
| 2 | 2 | 1:1:0 | 120 | 28 | > 99 | 9.7 | 1.93 | 267 |
| 3 | 3 | 1:1:0 | 120 | Trace | — | — | — | — |
| 4 | 4–6 | 1:1:0 | 120 | 0 | — | — | — | — |
| 5 | 1 | 1:1:10 | 20 | > 99 | > 99 | 14.5 | 2.15 | 271 |
| 6 | 2 or 3 | 1:1:10 | 120 | Trace | — | — | — | — |
| 7 | 4 | 1:1:10 | 120 | 80 | > 99 | 11.6 | 2.15 | 270 |
| 8 | 5 | 1:1:10 | 120 | 31 | > 99 | 8.2 | 2.27 | 266 |
| 9 | 6 | 1:1:10 | 120 | Trace | — | — | — | — |

^a Polymerization conditions: in toluene; [M]/[Ln] = 500; Ln, 21 μmol; solvent/monomer = 1:1 (v/v); T_p = 25 °C. ^b [B] = [Ph₃C][B(C₆F₅)₄]. ^c Yield = weight of polymer obtained/weight of monomer used. ^d Percentage of polymer insoluble in refluxing 2-butanone; *rrrr* > 99%, determined by ¹³C NMR in 1,1,2,2-C₂D₂Cl₄. ^e Determined by GPC in 1,2,4-trichlorobenzene at 145 °C against polystyrene standard. ^f Determined by DSC.

Conclusion

In summary, a new series of neutral, thermally stable, and unsolvated half-sandwich rare-earth-metal bis(silylamide) and bis(allyl) complexes bearing the pyrrolidinyl-functionalized cyclopentadienyl ligand were prepared and well-characterized. These neutral rare-earth-metal derivatives alone showed no activity toward styrene polymerization; however, upon activation with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, the bis(allyl) complexes became active while the bis(silylamide) complexes were still inert for styrene polymerization. Addition of excess Al^iBu_3 to the half-sandwich rare-earth-metal derivative/ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ binary catalyst systems improved the polymerization activity. The effects of central metals and active groups on the polymerization were strikingly obvious, with the scandium complexes and the rare-earth-metal allyl complexes showing relatively higher activity. These polymerizations afforded pure syndiotactic polystyrene with high syndiotacticity ($r_{\text{rrrr}} > 99\%$).

Experimental

Materials and procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques and an argon-filled glovebox. Solvents (toluene, hexane, and THF) were distilled from sodium/benzophenone ketyl, degassed by the freeze-pump-thaw method, and dried over fresh Na chips in the glovebox. Anhydrous LnCl_3 , $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ were purchased from Strem. Al^iBu_3 (1.1 M in toluene) and $\text{C}_3\text{H}_5\text{MgCl}$ (1.7 M in THF) were purchased from Acros, and used as received. $\text{HN}(\text{SiHMe}_2)_2$ was purchased from Fluoro Chem and used as received. $\text{C}_5\text{Me}_4\text{HSiMe}_2\text{Cl}$ and pyrrole were purchased from Aldrich, and used as received. Styrene was dried by stirring with CaH_2 , and distilled before polymerization. Deuterated solvents (CDCl_3 , C_6D_6 , $1,1,2,2\text{-C}_2\text{D}_2\text{Cl}_4$) were obtained from Aldrich.

Samples of rare-earth-metal complexes for NMR spectroscopic measurements were prepared in the glovebox using J. Young valve NMR tubes. NMR (^1H , ^{13}C) spectra were recorded on a Bruker AVANCE III spectrometer at 25 °C for the rare-earth-metal complexes and 120 °C for the polymer samples, and referenced internally to residual solvent resonances unless otherwise stated. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument. FT-IR spectra were recorded on a Bruker TENSOR 27 spectrometer. Molecular weight and molecular weight distribution of the polymers were measured by PL GPC 220 at 145 °C using 1,2,4-trichlorobenzene as eluent against polystyrene standards; flow rate: 1.0 mL min^{-1} , sample concentration: 1 mg mL^{-1} . The melting temperatures of the resulting polymers were measured on a NETZSCH DSC 200 PC instrument at a heating rate of 10 °C min^{-1} under N_2 atmosphere.

Syntheses

$\text{C}_5\text{Me}_4\text{HSiMe}_2\text{NC}_4\text{H}_8$. To a solution of $\text{C}_5\text{Me}_4\text{HSiMe}_2\text{Cl}$ (1.074 g, 5.00 mmol) in THF (20 mL) was added slowly one equiv. amount of $\text{C}_4\text{H}_8\text{NLi}$ (0.385 g, 5.00 mmol) prepared

from the reaction of $\text{C}_4\text{H}_9\text{N}$ with 1 equivalent of $n\text{-BuLi}$ in THF at room temperature. The mixture was stirred at room temperature for 1 d, and then the volatiles were removed *in vacuo*. The resulting white residue was extracted by hexane (50 mL) and filtered. Removal of hexane gave the desired product as a pale yellow oil (1.19 g, 95%). GC-Mass: > 99% purity, $m/z = 249$. ^1H NMR (400 MHz, C_6D_6): δ 0.07 (s, 6H, SiMe_2), 1.54 (m, 4H, $\text{C}_4\text{H}_8\text{N}$), 1.86 (br s, 6H, C_5Me_4), 1.99 (s, 6H, C_5Me_4), 2.87 (m, 4H, $\text{C}_4\text{H}_8\text{N}$), 2.96 (s, 1H, $\text{C}_5\text{Me}_4\text{H}$). ^{13}C NMR (100 MHz, C_6D_6): δ -3.1 (SiMe_2), 11.5 (C_5Me_4), 14.4 (C_5Me_4), 27.2 ($\text{C}_4\text{H}_8\text{N}$), 47.4 ($\text{C}_4\text{H}_8\text{N}$). FT-IR (KBr, cm^{-1}): 2962 (s), 2914 (s), 2858 (s), 1660 (w), 1444 (m), 1351 (m), 1249 (s), 1219 (m), 1120 (s), 1075 (s), 826 (s), 777 (m), 645 (m). Anal. Calcd for $\text{C}_{15}\text{H}_{27}\text{NSi}$: C, 72.22; H, 10.91; N, 5.61. Found: C, 72.19; H, 10.73; N, 5.77.

$(\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8)\text{Sc}(\eta^3\text{-C}_3\text{H}_5)_2$ (1). To a THF slurry of ScCl_3 (0.151 g, 1.00 mmol) was added slowly 1 equiv. of $\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8\text{Li}$ (0.255 g, 1.00 mmol) at room temperature ($\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8\text{Li}$ was prepared by the treatment of $\text{C}_5\text{Me}_4\text{HSiMe}_2\text{NC}_4\text{H}_8$ with one equiv. amount of $\text{LiCH}_2\text{-SiMe}_3$ in diethyl ether). The mixture was stirred at room temperature for 4 h to afford a clear solution, to which $\text{C}_3\text{H}_5\text{MgCl}$ (2.04 mmol, 1.7 M in THF) was introduced *via* a syringe. The resulting yellow solution was stirred at room temperature overnight. Removal of the volatiles gave a yellow residue, which was extracted by hexane ($3 \times 10\text{ mL}$). After filtration and removal of hexane, the crude product **1** was obtained as a yellow powder. Recrystallization from pentane at -20 °C gave **1** as yellow block crystals (0.244 g, 65%). ^1H NMR (400 MHz, C_6D_6): δ 0.24 (s, 6H, SiMe_2), 1.54 (m, 4H, $\text{C}_4\text{H}_8\text{N}$), 1.77 (s, 6H, C_5Me_4), 2.31 (s, 6H, C_5Me_4), 2.83 (m, 4H, $\text{C}_4\text{H}_8\text{N}$), 3.37 (d, $J = 12.4\text{ Hz}$, 8H, CH_2CHCH_2), 7.13 (m, 2H, CH_2CHCH_2). ^{13}C NMR (100 MHz, C_6D_6): δ 0.8 (SiMe_2), 11.9 (C_5Me_4), 15.4 (C_5Me_4), 27.2 ($\text{C}_4\text{H}_8\text{N}$), 47.2 ($\text{C}_4\text{H}_8\text{N}$), 79.0 (CH_2CHCH_2), 120.1 (C_5Me_4), 125.4 (C_5Me_4), 130.8 (C_5Me_4), 157.5 (CH_2CHCH_2). FT-IR (KBr, cm^{-1}): 3425 (m), 2963 (s), 2919 (s), 2864 (m), 1634 (m), 1530 (m), 1506 (m), 1477 (m), 1455 (m), 1382 (m), 1248 (m), 1109 (w), 1077 (w), 988 (m), 828 (m), 774 (m). Anal. Calcd for $\text{C}_{21}\text{H}_{36}\text{NScSi}$: C, 67.16; H, 9.66; N, 3.73. Found: C, 67.29; H, 9.45; N, 3.70.

$(\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8)\text{Y}(\eta^3\text{-C}_3\text{H}_5)_2$ (2). Following the same procedure as for **1**, YCl_3 (0.196 g, 1.00 mmol), $\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8\text{Li}$ (0.255 g, 1.00 mmol) and $\text{C}_3\text{H}_5\text{MgCl}$ (2.04 mmol, 1.7 M in THF) afforded the desired product as pale yellow crystals (0.223 g, 53%). ^1H NMR (400 MHz, C_6D_6): δ 0.24 (s, 6H, SiMe_2), 1.15 (s, 4H, $\text{C}_4\text{H}_8\text{N}$), 1.97 (m, 6H, C_5Me_4), 2.09 (s, 6H, C_5Me_4), 2.48 (m, 4H, $\text{C}_4\text{H}_8\text{N}$), 3.01 (d, $J = 12.4\text{ Hz}$, 8H, CH_2CHCH_2), 6.33 (m, 2H, CH_2CHCH_2). ^{13}C NMR (100 MHz, C_6D_6): δ 1.1 (SiMe_2), 12.0 (C_5Me_4), 14.8 (C_5Me_4), 25.3 ($\text{C}_4\text{H}_8\text{N}$), 51.3 ($\text{C}_4\text{H}_8\text{N}$), 69.3 (CH_2CHCH_2), 122.1 (C_5Me_4), 124.1 (C_5Me_4), 148.6 (CH_2CHCH_2). FT-IR (KBr, cm^{-1}): 3424 (m), 2964 (s), 2922 (s), 2870 (s), 1640 (w), 1534 (m), 1503 (m), 1475 (m), 1452 (s), 1382 (m), 1250 (s), 1078 (m), 918 (m), 829 (m), 778 (m). Anal. Calcd for $\text{C}_{21}\text{H}_{36}\text{NSiY}$: C, 60.12; H, 8.65; N, 3.34. Found: C, 59.98; H, 8.42; N, 3.51.

$(\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8)\text{Lu}(\eta^3\text{-C}_3\text{H}_5)_2$ (3). Following the same procedure as for **1**, LuCl_3 (0.282 g, 1.00 mmol), $\text{C}_5\text{Me}_4\text{SiMe}_2\text{-NC}_4\text{H}_8\text{Li}$ (0.255 g, 1.00 mmol) and $\text{C}_3\text{H}_5\text{MgCl}$ (2.04 mmol, 1.7 M

in THF) afforded the desired product as a pale green solid (0.268 g, 53%). ^1H NMR (400 MHz, C_6D_6): δ 0.22 (s, 6H, SiMe_2), 1.15 (m, 4H, $\text{C}_4\text{H}_8\text{N}$), 1.94 (s, 6H, C_5Me_4), 2.13 (s, 6H, C_5Me_4), 2.52 (m, 4H, $\text{C}_4\text{H}_8\text{N}$), 3.05 (d, $J = 12.4$ Hz, 8H, CH_2CHCH_2), 6.47 (m, 2H, CH_2CHCH_2). ^{13}C NMR (100 MHz, C_6D_6): δ 1.1 (SiMe_2), 11.9 (C_5Me_4), 14.8 (C_5Me_4), 25.3 ($\text{C}_4\text{H}_8\text{N}$), 51.1 ($\text{C}_4\text{H}_8\text{N}$), 69.2 (CH_2CHCH_2), 121.9 (C_5Me_4), 123.6 (C_5Me_4), 150.8 (CH_2CHCH_2). FT-IR (KBr, cm^{-1}): 3424 (s), 2964 (s), 2924 (s), 2871 (m), 1640 (w), 1531 (m), 1505 (m), 1475 (m), 1453 (m), 1382 (w), 1250 (m), 1078 (m), 918 (m), 829 (m), 778 (m). Anal. Calcd for $\text{C}_{21}\text{H}_{36}\text{LuNSi}$: C, 49.89; H, 7.18; N, 2.77. Found: C, 49.79; H, 7.03; N, 2.96.

($\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8$)Sc[N(SiHMe $_2$) $_2$] (4**).** To a THF slurry of ScCl_3 (0.151 g, 1.00 mmol) was added slowly 1 equivalent of $\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8\text{Li}$ (0.255 g, 1.00 mmol) at room temperature. The mixture was stirred at room temperature for 4 h to afford a clear colorless solution, to which $\text{LiN}(\text{SiHMe}_2)_2$ (0.279 g, 2.00 mmol) was added at room temperature. The resulting pale yellow solution was stirring at room temperature for 24 h. Remove of the volatiles gave a white residue, which was extracted with hexane. The extractant was filtrated and concentrated to afford a pale yellow oil. Recrystallization from hexane at -20°C gave **4** as a white crystalline solid (0.346 g, 62%). ^1H NMR (400 MHz, C_6D_6): δ 0.28 (br s, 24H, SiHMe_2), 0.62 (s, 6H, SiMe_2), 1.54 (m, 4H, $\text{C}_4\text{H}_8\text{N}$), 2.12 (s, 6H, C_5Me_4), 2.43 (s, 6H, C_5Me_4), 2.83 (m, 4H, $\text{C}_4\text{H}_8\text{N}$), 4.51 (m, 4H, SiHMe_2). ^{13}C NMR (100 MHz, C_6D_6): δ 2.0 (SiMe_2), 3.1 (SiHMe_2), 12.4 (C_5Me_4), 15.3 (C_5Me_4), 27.2 ($\text{C}_4\text{H}_8\text{N}$), 47.2 ($\text{C}_4\text{H}_8\text{N}$), 119.7 (C_5Me_4), 126.4 (C_5Me_4), 132.1 (C_5Me_4). FT-IR (KBr, cm^{-1}): 3423(m), 2963 (s), 2920 (m), 2876 (m), 2120 (w), 1632 (w), 1506 (s), 1478 (m), 1455 (s), 1382 (w), 1249 (s), 1109 (w), 985 (s), 908 (s), 827 (s), 773 (s). Anal. Calcd for $\text{C}_{23}\text{H}_{54}\text{N}_3\text{ScSi}_5$: C, 49.50; H, 9.75; N, 7.53. Found: C, 49.62; H, 9.71; N, 7.48.

($\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8$)Y[N(SiHMe $_2$) $_2$] (5**).** Following the same procedure as for **4**, YCl_3 (0.196 g, 1.00 mmol), $\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8\text{Li}$ (0.255 g, 1.00 mmol), and $\text{LiN}(\text{SiHMe}_2)_2$ (0.279 g, 2.00 mmol) afforded **5** as colorless crystals (0.362 g, 60%). ^1H NMR (400 MHz, C_6D_6): δ 0.34 (d, $J = 2.8$ Hz, 24H, SiHMe_2), 0.38 (s, 6H, SiMe_2), 1.34 (m, 4H, $\text{C}_4\text{H}_8\text{N}$), 2.24 (s, 6H, C_5Me_4), 2.33 (s, 6H, C_5Me_4), 2.91 (m, 4H, $\text{C}_4\text{H}_8\text{N}$), 4.66 (m, 4H, SiHMe_2). ^{13}C NMR (100 MHz, C_6D_6): δ 1.5 (SiMe_2), 3.4 (SiHMe_2), 12.5 (C_5Me_4), 15.1 (C_5Me_4), 25.8 ($\text{C}_4\text{H}_8\text{N}$), 50.7 ($\text{C}_4\text{H}_8\text{N}$), 105.5 (C_5Me_4), 125.8 (C_5Me_4), 126.3 (C_5Me_4). FT-IR (KBr, cm^{-1}): 3386 (m), 2961 (s), 2915 (m), 2875 (m), 2120 (m), 1664 (w), 1626 (w), 1535 (m), 1501 (m), 1474 (m), 1455 (m), 1384 (m), 1252 (s), 1179 (m), 1068 (s), 1024 (s), 910 (s), 825 (s), 793 (s), 653 (m). Anal. Calcd for $\text{C}_{23}\text{H}_{54}\text{N}_3\text{Si}_5\text{Y}$: C, 45.88; H, 9.04; N, 6.98. Found: C, 46.05; H, 8.97; N, 7.04.

($\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8$)Lu[N(SiHMe $_2$) $_2$] (6**).** Following the same procedure as for **4**, LuCl_3 (0.282 g, 1.00 mmol), $\text{C}_5\text{Me}_4\text{SiMe}_2\text{NC}_4\text{H}_8\text{Li}$ (0.255 g, 1.00 mmol), and $\text{LiN}(\text{SiHMe}_2)_2$ (0.279 g, 2.00 mmol) afforded **6** as colorless crystals (0.351 g, 51%). ^1H NMR (400 MHz, C_6D_6): δ 0.33 (s, 24H, SiHMe_2), 0.50 (s, 6H, SiMe_2), 1.45 (m, 4H, $\text{C}_4\text{H}_8\text{N}$), 2.19 (s, 6H, C_5Me_4), 2.42 (s, 6H, C_5Me_4), 2.90 (m, 4H, $\text{C}_4\text{H}_8\text{N}$), 4.67 (s, 4H, SiHMe_2). ^{13}C NMR (100 MHz, C_6D_6): δ 1.9 (SiMe_2), 3.4 (SiHMe_2), 12.2 (C_5Me_4),

14.9 (C_5Me_4), 26.6 ($\text{C}_4\text{H}_8\text{N}$), 48.9 ($\text{C}_4\text{H}_8\text{N}$), 111.4 (C_5Me_4), 125.1 (C_5Me_4). FT-IR (KBr, cm^{-1}): 3389 (m), 2961 (s), 2918 (m), 2873 (m), 2120 (m), 1631 (w), 1537 (m), 1505 (m), 1453 (m), 1405 (w), 1381 (w), 1252 (s), 1178 (m), 1024 (m), 908 (s), 827 (m), 792 (m), 652 (m). Anal. Calcd for $\text{C}_{23}\text{H}_{54}\text{LuN}_3\text{Si}_5$: C, 40.15; H, 7.91; N, 6.11. Found: C, 40.30; H, 7.89; N, 6.25.

Styrene polymerization

The procedures for styrene polymerization catalyzed by these complexes were similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask equipped with a magnetic stirring bar was charged in sequence with the desired amount of rare-earth-metal complex, $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, toluene, (Al^iBu_3) , and styrene. The mixture was stirred vigorously at room temperature for the desired time, during which the polymer precipitation was observed. The reaction mixture was quenched by addition of a large amount of ethanol to precipitate the polymer, which was dried under vacuum at 60°C to constant weight.

Solvent extraction

Solvent fractionation was carried out using a 100 mL Soxhlet extractor.¹⁰ 1.0 g of polystyrene sample was placed in a cellulose thimble and extracted successively with 50 mL of boiling methyl ethyl ketone for 4 h. After that, the solvent was evaporated under vacuum, and the residue in the thimble was dried under vacuum at 60°C to constant weight.

X-Ray crystallographic study

Suitable single crystals of the rare-earth-metal complexes were sealed in a thin-walled glass capillary for determining the single crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71070 \text{ \AA}$). The diffracted intensities were corrected for Lorentz-polarization effects and empirical absorption corrections. The structures were solved by direct methods, and refined by full-matrix least-squares procedures based on $|F|^2$. All the non-hydrogen atoms were refined anisotropically. The structures were solved and refined using SHELXL-97 program. CCDC 917594–917599 contains the supplementary crystallographic data for **1–6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21172195). We are grateful to Mr Yong Zhang at Suzhou University for X-ray analysis help.

References

- (a) F. T. Edelmann, *Coord. Chem. Rev.*, 2012, **256**, 1151; (b) M. Zimmermann and R. Anwender, *Chem. Rev.*, 2010, **110**, 6194; (c) M. Nishiura and Z. M. Hou, *Nat. Chem.*, 2010, **2**, 257; (d) P. M. Zeimentz, S. Arndt, B. R. Elvidge and

- J. Okuda, *Chem. Rev.*, 2006, **106**, 2404; (e) H. B. Li and T. J. Marks, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15295; (f) J. Gromada, J. F. Carpentier and A. Mortreux, *Coord. Chem. Rev.*, 2004, **248**, 397; (g) F. T. Edelmann, D. M. M. Freckmann and H. Schumann, *Chem. Rev.*, 2002, **102**, 1851; (h) G. A. Molander and J. A. C. Romero, *Chem. Rev.*, 2002, **102**, 2161; (i) W. J. Evans and B. L. Davis, *Chem. Rev.*, 2002, **102**, 2119; (j) W. E. Piers and D. J. H. Emsile, *Coord. Chem. Rev.*, 2002, **233**, 131; (k) H. Schumann, J. A. Meese-Marktscheffel and L. Esser, *Chem. Rev.*, 1995, **95**, 865.
- 2 (a) R. Litlabø, M. Enders, K. W. Törnroos and R. Anwänder, *Organometallics*, 2010, **29**, 2588; (b) M. Zimmermann, J. Volbeda, K. W. Törnroos and R. Anwänder, *C. R. Chim.*, 2010, **13**, 651; (c) M. Zimmermann, K. W. Törnroos and R. Anwänder, *Angew. Chem., Int. Ed.*, 2008, **47**, 775; (d) M. Zimmermann, K. W. Törnroos, H. Sitzmann and R. Anwänder, *Chem.-Eur. J.*, 2008, **14**, 7266; (e) E. L. Roux, F. Nief, F. Jaroschik, K. W. Törnroos and R. Anwänder, *Dalton Trans.*, 2007, **36**, 4866; (f) S. Arndt, B. R. Elvidge, P. M. Zeimentz, T. P. Spaniol and J. Okuda, *Organometallics*, 2006, **25**, 793; (g) P. G. Hayes, W. E. Piers and M. Parvez, *Organometallics*, 2005, **24**, 1173; (h) H. M. Dietrich, C. Zapilko, E. Herdtweck and R. Anwänder, *Organometallics*, 2005, **24**, 5767; (i) L. D. Henderson, G. D. MacInnis, W. E. Piers and M. Parvez, *Can. J. Chem.*, 2004, **82**, 162; (j) P. G. Hayes, W. E. Piers and M. Parvez, *J. Am. Chem. Soc.*, 2003, **125**, 5622; (k) R. Anwänder, M. G. Klimpel, H. M. Dietrich, D. J. Shorokhov and W. Scherer, *Chem. Commun.*, 2003, 1008; (l) P. G. Hayes, W. E. Piers and R. McDonald, *J. Am. Chem. Soc.*, 2002, **124**, 2132.
- 3 (a) S. Ge, A. Meetsma and B. Hessen, *Organometallics*, 2009, **28**, 719; (b) N. Meyer, P. W. Roesky, M. Bamber, A. Meetsma, B. Hessen, K. Saliu and J. Takats, *Organometallics*, 2008, **27**, 1501; (c) S. Bamber, F. Perazzolo, S. J. Boot, T. J. J. Sciarone, A. Meetsma and B. Hessen, *Organometallics*, 2008, **27**, 704; (d) C. T. Carver, M. J. Monreal and P. L. Diaconescu, *Organometallics*, 2008, **27**, 363; (e) S. Bamber, A. Meetsma and B. Hessen, *Organometallics*, 2006, **25**, 3454; (f) L. W. M. Lee, W. E. Piers, M. R. J. Elsegood, W. Clegg and M. Parvez, *Organometallics*, 1999, **18**, 2947.
- 4 For examples, see: (a) Z. B. Jian, A. R. Petrov, N. K. Hangaly, S. H. Li, W. F. Rong, Z. H. Mou, K. A. Ruffanov, K. Harms, J. Sundermeyer and D. M. Cui, *Organometallics*, 2012, **31**, 4267; (b) B. Royo and E. Peris, *Eur. J. Inorg. Chem.*, 2012, 1309; (c) Z. B. Jian, D. M. Cui and Z. M. Hou, *Chem.-Eur. J.*, 2012, **18**, 2674; (d) Y. P. Pan, W. F. Rong, Z. B. Jian and D. M. Cui, *Macromolecules*, 2012, **45**, 1248; (e) Z. B. Jian and D. M. Cui, *Chem.-Eur. J.*, 2011, **17**, 14578; (f) C. Doring, W. P. Kretschmer and R. Kempe, *Eur. J. Inorg. Chem.*, 2010, 2853; (g) D. M. Lyubov, G. K. Fukin, A. V. Cherkasov, A. S. Shavyrin, A. A. Trifonov, L. Luconi, C. Bianchini, A. Meli and G. Giambastiani, *Organometallics*, 2009, **28**, 1227; (h) D. M. Lyubov, C. Doring, G. K. Fukin, A. V. Cherkasov, A. S. Shavyrin, R. Kempe and A. A. Trifonov, *Organometallics*, 2008, **27**, 2905; (i) T. K. Panda, C. G. Hrib, P. G. Jones, J. Jenter, P. W. Roesky and M. Tamm, *Eur. J. Inorg. Chem.*, 2008, 4270; (j) A. Ravasio, C. Zampa, L. Boggioni, I. Tritto, J. Hitzbleck and J. Okuda, *Macromolecules*, 2008, **41**, 9565; (k) L. X. Zhang, T. Suzuki, Y. Luo, M. Nishiura and Z. M. Hou, *Angew. Chem., Int. Ed.*, 2007, **46**, 1909; (l) X. F. Li, J. Baldamus, M. Nishiura, O. Tardif and Z. M. Hou, *Angew. Chem., Int. Ed.*, 2006, **45**, 8184; (m) L. X. Zhang, Y. Luo and Z. M. Hou, *J. Am. Chem. Soc.*, 2005, **127**, 14562; (n) X. F. Li, J. Baldamus and Z. M. Hou, *Angew. Chem., Int. Ed.*, 2005, **44**, 962; (o) C. S. Tredget, F. Bonnet, A. R. Cowley and P. Mountford, *Chem. Commun.*, 2005, 3301; (p) X. F. Li and Z. M. Hou, *Macromolecules*, 2005, **38**, 6767; (q) B. D. Ward, S. Bellemin-Lapponnaz and L. H. Gade, *Angew. Chem., Int. Ed.*, 2005, **44**, 1668; (r) B. R. Elvidge, S. Arndt, P. M. Zeimentz, T. P. Spaniol and J. Okuda, *Inorg. Chem.*, 2005, **44**, 6777; (s) Y. J. Luo, J. Baldamus and Z. M. Hou, *J. Am. Chem. Soc.*, 2004, **126**, 13910; (t) S. Bamber, M. W. Bouwkamp, A. Meetsma and B. Hessen, *J. Am. Chem. Soc.*, 2004, **126**, 9182; (u) S. Arndt, T. P. Spaniol and J. Okuda, *Angew. Chem., Int. Ed.*, 2003, **42**, 5075; (v) S. C. Lawrence, B. D. Ward, S. R. Dubberley, C. M. Kozak and P. Mountford, *Chem. Commun.*, 2003, 2880; (w) S. Arndt, T. P. Spaniol and J. Okuda, *Chem. Commun.*, 2002, 896; (x) S. Bamber, D. van Leusen, A. Meetsma, B. Hessen and J. H. Teuben, *Chem. Commun.*, 2001, 637.
- 5 (a) Z. B. Jian, D. M. Cui, Z. M. Hou and X. F. Li, *Chem. Commun.*, 2010, **46**, 3022; (b) Z. B. Jian, S. J. Tang and D. M. Cui, *Chem.-Eur. J.*, 2010, **16**, 14007; (c) Z. B. Jian, W. Zhao, X. L. Liu, X. S. Chen, T. Tang and D. M. Cui, *Dalton Trans.*, 2010, **39**, 6871; (d) X. F. Li, M. Nishiura, L. H. Hu, K. Mori and Z. M. Hou, *J. Am. Chem. Soc.*, 2009, **131**, 13870; (e) B. L. Wang, D. M. Cui and K. Lv, *Macromolecules*, 2008, **41**, 1983; (f) A. Otero, J. Fernández-Baeza, A. Antiñolo, A. Lara-Sánchez, E. Martínez-Caballero, J. Tejeda, L. F. Sánchez-Barba, C. Alonso-Moreno and I. López-Solera, *Organometallics*, 2008, **27**, 976; (g) B. L. Wang, D. Wang, D. M. Cui, W. Gao, T. Tang, X. S. Chen and X. B. Jing, *Organometallics*, 2007, **26**, 3167; (h) J. Hitzbleck and J. Okuda, *Organometallics*, 2007, **26**, 3227; (i) K. A. Ruffanov, A. R. Petrov, V. V. Kotov, F. Laquai and J. Sundermeyer, *Eur. J. Inorg. Chem.*, 2005, 3805; (j) S. Arndt, T. P. Spaniol and J. Okuda, *Organometallics*, 2003, **22**, 775; (k) D. J. Beetstra, A. Meetsma, B. Hessen and J. H. Teuben, *Organometallics*, 2003, **22**, 4372; and ref. 2a,4a-d,4i.
- 6 (a) F. Guo, M. Nishiura, H. Koshino and Z. M. Hou, *Macromolecules*, 2011, **44**, 2400; (b) L. F. Wang, D. M. Cui, Z. M. Hou, W. Li and Y. Li, *Organometallics*, 2011, **30**, 760; (c) W. X. Zhang, M. Nishiura, T. Mashiko and Z. M. Hou, *Chem.-Eur. J.*, 2008, **14**, 2167; (d) M. Nishiura, T. Mashiko and Z. M. Hou, *Chem. Commun.*, 2008, 2019; (e) X. F. Li, M. Nishiura, K. Mori, T. Mashiko and Z. M. Hou, *Chem. Commun.*, 2007, 4137; (f) F. Jaroschik, T. Shima, X. F. Li, K. Mori, L. Ricard, X. F. L. Goff, F. Nief and Z. M. Hou, *Organometallics*, 2007, **26**, 5654; (g) S. Harder,

- Organometallics*, 2005, **24**, 373; (h) L. E. Manzer, *J. Am. Chem. Soc.*, 1978, **100**, 8068; and ref. 4c.
- 7 (a) D. Robert, E. Abinet, T. Spaniol and J. Okuda, *Chem.-Eur. J.*, 2009, **15**, 11937; (b) N. Yu, M. Nishiura, X. F. Li, Z. F. Xi and Z. M. Hou, *Chem.-Asian J.*, 2008, **3**, 1406; (c) R. Taube, S. Maiwald and J. Sieler, *J. Organomet. Chem.*, 2001, **621**, 327; and ref. 4c, 5a–b.
- 8 (a) Y. J. Luo, Y. L. Lei, S. M. Fan, Y. B. Wang and J. Chen, *Dalton Trans.*, 2013, **42**, 4040; (b) Y. B. Wang, Y. L. Lei, S. H. Chi and Y. J. Luo, *Dalton Trans.*, 2013, **42**, 1862; (c) F. Chen, S. M. Fan, Y. B. Wang, J. Chen and Y. J. Luo, *Organometallics*, 2012, **31**, 3730; (d) Y. B. Wang, Y. J. Luo, J. Chen, H. M. Xue and H. Z. Liang, *New J. Chem.*, 2012, **36**, 933; (e) Y. J. Luo, X. Y. Feng, Y. B. Wang, S. M. Fan, J. Chen, Y. L. Lei and H. Z. Liang, *Organometallics*, 2011, **30**, 3270; (f) Y. J. Luo, S. M. Fan, J. P. Yang, J. H. Fang and P. Xu, *Dalton Trans.*, 2011, **40**, 3053; (g) Y. J. Luo, P. Xu, Y. L. Lei, Y. Zhang and Y. R. Wang, *Inorg. Chim. Acta*, 2010, **363**, 3597.
- 9 R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.*, 1976, **32**, 751.
- 10 G. X. Xu and S. A. Lin, *Macromolecules*, 1997, **30**, 685.