



Syndio-specific polymerization of styrene promoted by rare-earth metal bis(aminobenzyl) complexes bearing pyrrolyl-modified arylamide ligands

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ABSTRACT

Acid-base reaction of the rare-earth metal tris(*o*-dimethylaminobenzyl) complexes Ln (CH₂C₆H₄NMe₂-*o*)₃ with 1 equiv. of the pyrrolyl-modified arylamide ligands 2,5-Me₂C₄H₂NSiMe₂NHC₆H₄R (R = H, Cl-*p*, OMe-*p*) in toluene gave (2,5-Me₂C₄H₂NSiMe₂NC₆H₅)Ln (CH₂C₆H₄NMe₂-*o*)₂ (Ln = Sc (**1**), Y (**2**), Lu (**3**)), (2,5-Me₂C₄H₂NSiMe₂NC₆H₄Cl-*p*)Y(CH₂C₆H₄NMe₂-*o*)₂ (**4**), and (2,5-Me₂C₄H₂NSiMe₂NC₆H₄OMe-*p*)Y(CH₂C₆H₄NMe₂-*o*)₂ (**5**) in good isolated yields. These complexes were well-characterized by elemental analysis and NMR spectroscopy. **1**, **2** and **4** were structurally determined by single crystal X-ray diffraction. The catalyst systems of **1–5**/AlⁱBu₃/[Ph₃C][B(C₆F₅)₄] were able to promote styrene polymerization to afford pure and highly syndio-tactic polystyrene (*rrrr* > 99%). Among these rare-earth metal complexes, the complexes with the central metal being the cheapest yttrium showed much higher activity than the expensive scandium analogues. The styrene polymerization catalyzed by **4**/AlⁱBu₃/[Ph₃C][B(C₆F₅)₄] proceeded in a controlled fashion.

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1. Introduction

Syndio-tactic polystyrene (sPS) is a very promising polymeric material because of its high melting point (*ca.* 270 °C), high crystallinity, high modulus of elasticity, low dielectric constant, and excellent resistance to heat and chemicals [1]. In 1986, Ishihara and co-workers at Idemitsu first discovered sPS using the homogeneous titanium catalyst systems Cp*TiCl₃/MAO [2]. For the highly reactive and coordination unsaturated rare-earth metals, rare-earth metal complexes should be stabilized by steric demanding ancillary ligands. Consequently, they are rather difficult to polymerize bulky monomers such as styrene. Encouragingly, Hou and Carpentier independently found that the cationic scandium catalyst system (C₅Me₄SiMe₃)Sc(CH₂SiMe₃)₂ (THF)/[Ph₃C][B(C₆F₅)₄] [3] and the neutral neodymium ally complex [FluCM₂Cp]Nd(C₃H₅) (THF) [4] could serve as highly active initiators for syndio-specific polymerization of styrene in 2004. From then on, the development of different kind of rare-earth metal complexes for syndio-specific styrene polymerization have attracted increasing attention [5–25], and it turned out that cationic rare-earth metal complexes

[LLn-R]⁺ (L = Cp and its derivatives, R = alkyl, benzyl or allyl groups) in which the central metal is the expensive scandium usually demonstrated high activity and selectivity [25]. Therefore, exploring the possibility of more abundant and much cheaper rare-earth-metal-based complexes for syndio-specific polymerization of styrene is a quite challenging but very attractive project from both academic and industry points of view.

Arylamide frameworks are easily accessible and their steric and electronic environments are ready to be tuned by the variation of substituents on both phenyl ring and nitrogen atom [26–36]. Schumann and co-workers firstly introduced this kind of non-Cp mono-dentate ligands into the field of rare-earth metal chemistry, and prepared a series of bis(arylamide) rare-earth metal chloride complexes and tris(arylamide) rare-earth metal complexes in 1995 [36]. Upon to date, the reactivity of arylamide-ligated rare-earth metal complexes are still far less explored [26,27,29,30,33,34]. Recently, we found that the rare-earth metal bis(alkyl) and bis(amide) complexes supported by arylamide ligands could exhibit promising reactivity in regio-selective polymerization of isoprene [26,29]. However, these rare-earth metal complexes showed poor activity and stereo-selectivity toward styrene polymerization [29]. To further explore the structure-reactivity of such kind of rare-earth metal complexes, we extended our interest to rare-earth

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metal complexes stabilized by pyrrolyl-modified arylamide ligands, envisaging the neutral pendant pyrrolyl moiety would tune Lewis acidity and effective coordination sphere at the central metal. It was found that subtle modification of the arylamide scaffolds led to strikingly different reaction pattern of the resulting rare-earth metal complexes, and the yttrium bis(aminobenzyl) complexes ligated by pyrrolyl-modified arylamides showed much higher activity toward syndio-specific polymerization of styrene than the expensive scandium analogues. This finding is of great interest to develop cheap rare-earth metal catalysts for syndio-specific polymerization of styrene. Here we report these results.

2. Results and discussion

2.1. Ligand synthesis

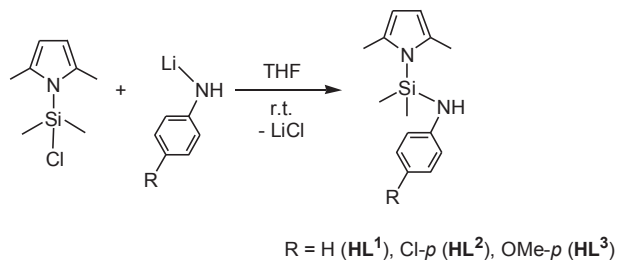
Treatment of 2,5-Me₂C₄H₂NSiMe₂Cl (separated from the reaction of 2,5-Me₂C₄H₂NLi with excess SiMe₂Cl₂ in hexane) with one equivalent of LiNHC₆H₄R in THF at ambient temperature produced 2,5-Me₂C₄H₂NSiMe₂NHC₆H₄R (R = H (**HL**¹), Cl-*p* (**HL**²), OMe-*p* (**HL**³)) in good isolated yields (Scheme 1). These pyrrolyl-modified arylamide ligands were well-characterized by elemental analysis and NMR spectroscopy.

2.2. Synthesis and characterization of the pyrrolyl-arylamide rare-earth metal bis(aminobenzyl) complexes

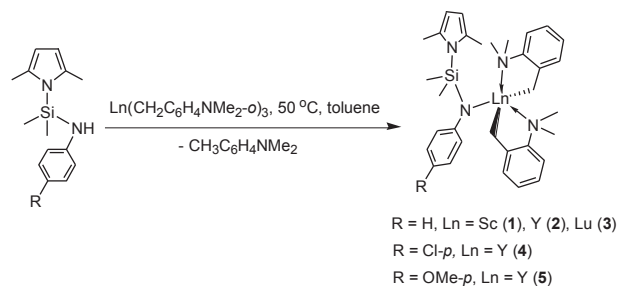
Acid-base reaction of the rare-earth metal tris(*o*-dimethylaminobenzyl) complexes Ln(CH₂C₆H₄NMe₂-*o*)₃ with 1 equiv. of the arylamide ligands 2,5-Me₂C₄H₂NSiMe₂NHC₆H₄R (R = H (**HL**¹), Cl-*p* (**HL**²), OMe-*p* (**HL**³)) at 50 °C in toluene, after workup, afforded L¹Ln(CH₂C₆H₄NMe₂-*o*)₂ (Ln = Sc (**1**), Y (**2**), Lu (**3**)), L²Y(CH₂C₆H₄NMe₂-*o*)₂ (**4**) and L³Y(CH₂C₆H₄NMe₂-*o*)₂ (**5**), as shown in Scheme 2.

All these complexes were characterized by elemental analysis and NMR spectroscopy. They are soluble in toluene, but sparingly soluble in hexane. In ¹H NMR spectra, the pyrrolyl ring protons show one singlet at 6.04 ppm for **1**, 6.02 ppm for **2**, 6.05 ppm for **3**, 5.99 ppm for **4**, 6.05 ppm for **5**, which are hardly chemical shifted compared to those of the corresponding ligands **HL**¹ (δ 6.09 ppm), **HL**² (δ 6.09 ppm), and **HL**³ (δ 6.14 ppm), suggestive of no direct interaction between the pendant pyrrolyl moiety and central metal.

To reveal the coordination situation of these rare-earth metal complexes, single crystal X-ray diffraction of **1**, **2** and **4** were performed. Single crystals of these complexes suitable for X-ray diffraction were grown from a mixture solution of toluene and hexane at -30 °C. The molecular structures of **1**, **2** and **4** with selected bond distances and bond angles are illustrated in (Figs. 1–3), respectively. Since X-ray diffraction showed these complexes are isomorphous, only the molecular structure of **4** is discussed in detail. As shown in (Fig. 3), the centre metal Y³⁺ in **4** is five-coordinated to an arylamide ligand through the nitrogen atom



Scheme 1. Ligand synthesis.



Scheme 2. Preparation of 1–5.

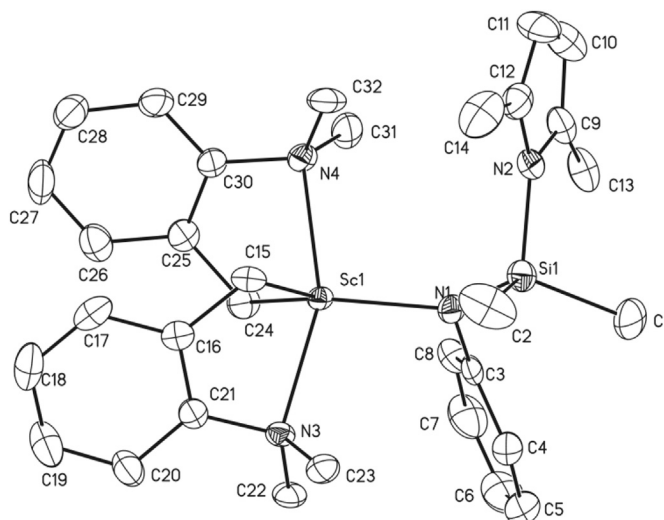


Fig. 1. Molecular structure of **1**. Selected bond distances (Å) and bond angles (°): Sc(1)–N (1) = 2.110 (5), Sc(1)–C (24) = 2.261 (6), Sc(1)–N (4) = 2.348 (5), Sc(1)–C (15) = 2.250 (6), Sc(1)–N (3) = 2.355 (4), Sc(1)–C (24) = 2.261 (6), C (24)–Sc(1)–N (4) = 74.49 (19), C (15)–Sc(1)–N (3) = 75.30 (18).

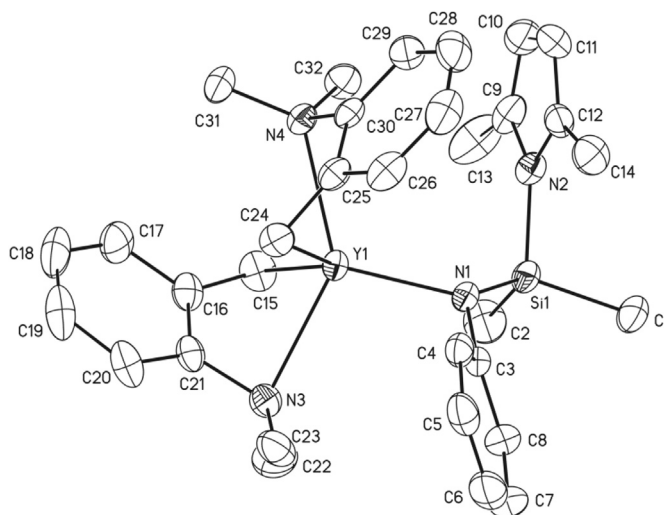


Fig. 2. Molecular structure of **2**. Selected bond distances (Å) and bond angles (°): Y (1)–N (1) = 2.2576 (17), Y (1)–C (3) = 2.846 (2), Y (1)–N (3) = 2.510 (2), Y (1)–C (15) = 2.439 (2), Y (1)–N (4) = 2.4726 (18), Y (1)–C (24) = 2.453 (2), C (15)–Y (1)–N (3) = 69.90 (8), C (24)–Y (1)–N (4) = 70.59 (7).

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