Dalton Transactions

PAPER

Cite this: Dalton Trans., 2013, 42, 16355

Received 24th July 2013, Accepted 9th September 2013 DOI: 10.1039/c3dt52014e

www.rsc.org/dalton

Introduction

Compared to monomeric complexes, bimetallic complexes are anticipated to exhibit a cooperative effect between two metal centers and/or nuclearity effects in organic transformation and polymerization.¹ Up to date, bimetallic complexes of main group and transition metals have received considerable attention and have displayed a unique reactivity and selectivity which is strikingly different to their mononuclear analogues.² For example, Marks *et al.* reported that the bimetallic titanium (Ti₂) and zirconium (Zr₂) complexes supported by "constrained geometry" ligands showed an obvious cooperative effect in olefin (co)polymerization.³ Harder and co-workers described that the bimetallic β -diketiminate-ligated calcium and zinc complexes were efficient catalysts for the copolymerization of cyclohexene oxide with CO₂.⁴ Messerle *et al.* reported that the

Synthesis of β -diketiminate-ligated bimetallic and monometallic lanthanide amide complexes and their reactivity with isoprene and AlMe₃†

Song Sun,^{a,b} Hao Ouyang,^a Yunjie Luo,^{*c} Yong Zhang,^a Qi Shen^a and Yingming Yao^{*a}

The amine elimination of lanthanide tris(amide) complexes with the phenylene-bridged bis(β -diketiminate) ligands PARA^{Me}-H₂, META^{Me}-H₂ and PARA^{Pr}-H₂ (PARA^{Me}-H₂ = 2[2,6-Me₂C₆H₃NHC(Me)C(H)C(Me)N]-(*para*-phenylene), META^{Me}-H₂ = 2[2,6-ⁱPr₂C₆H₃NHC(Me)C(H)C(Me)N]-(*meta*-phenylene), PARA^{Pr}-H₂ = 2[2,6-ⁱPr₂C₆H₃NHC(Me)C(H)C(Me)N]-(*para*-phenylene)), and the mono- β -diketiminate ligand L^{2,6-iPr2}_{Ph}-H (2,6-ⁱPr₂C₆H₃NHC(Me)C(H)C(Me)N]-(*para*-phenylene)), and the mono- β -diketiminate ligand L^{2,6-iPr2}_{Ph}-H (2,6-ⁱPr₂C₆H₃NHC(Me)C(Me)N(C₆H₅)) afforded the bimetallic lanthanide amide complexes PARA^{Me}-{Ln[N(SiMe₃)₂]₂} (Ln = Y (1), Sm (2)), META^{Me}-{Y[N(SiMe₃)₂]₂} (3), PARA^{Pr}-{Ln[N(HSiMe₂)₂]₂} (Ln = Y (4), Sm (5)), and the monomeric complexes L^{2,6-iPr2}_{Ph}-Y[N(SiMe₃)₂]₂ (6) and L^{2,6-iPr2}_{Ph}-Y[N(HSiMe₂)₂]₂ (7). In the presence of AlR₃ and on activation with 1 equiv. of [Ph₃C][B(C₆F₅)₄], complexes 1–7 showed a high activity toward the 1,4-selective polymerization of isoprene. The heterometallic Y/AI methyl complex [L^{2,6-iPr2}_{Ph}-P]Y[(µ-Me)₂AIMe₂]₂ (8) was prepared to elucidate the real active precursor in the polymerization.

bimetallic Rh(1) and/or Ir(1) pyrazolyl complexes were highly active for the intramolecular dihydroalkoxylation reaction of alkyne diol substrates.²ⁿ In contrast, the cooperative effect of bimetallic lanthanide complexes remains far less explored. To date, only quite limited bimetallic lanthanide derivatives have been reported, in which most complexes were employed as neutral initiators for the polymerization of polar monomers such as lactides.⁵ Whereas, bimetallic lanthanide complexes as cationic pre-catalysts remain scarce. Only one example with respect to isoprene polymerization using bimetallic lanthanide alkyl complexes has been reported while this paper is in preparation.⁶

Recently, we found that the phenylene-bridged bis(β -diketiminate) ligands are promising dinucleating ligand sets which stabilize the bimetallic lanthanide amide complexes, and these complexes are efficient initiators for the ring-opening polymerization of lactides.^{5h} To investigate the structure-reactivity relationship of the bimetallic lanthanide complexes in the polymerization, a series of new bimetallic lanthanide amide complexes stabilized by the rigid phenylene-bridged bis-(β-diketiminate) ligands was synthesized and characterized. It was found that these bimetallic lanthanide amide complexes could serve as highly active catalyst precursors in isoprene polymerization. The essential role of the lanthanide amide in the polymerization was also investigated. To our knowledge, this is the first example with respect to the investigation of isoprene polymerization employing bimetallic lanthanide amide complexes as pre-catalysts. Here we wish to report these results.

View Article Online

^aKey Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou 215123, People's Republic of China. E-mail: yaoym@suda.edu.cn; Fax: +(86) 512-65880305; Tel: +(86) 512-65882806

^bInstitute of Functional Material, School of Materials Science and Engineering, Shaanxi University of Technology, Hanzhong 723003, People's Republic of China ^cOrganometallic Chemistry Laboratory, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, P. R. China. E-mail: lyj@nit.zju.edu.cn

[†]Electronic supplementary information (ESI) available. CCDC numbers 952927 (for 1), 952928 (for 2), 952929 (for 3), 952930 (for 4), 952931 (for 6), 952932 (for 7) and 952933 (for 8). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52014e

Results and discussion

Synthesis and characterization

The amine elimination of $Ln[N(TMS)_2]_3(\mu-Cl)Li(THF)_3$ with PARA^{Me}-H₂, and META^{Me}-H₂ in a 2:1 molar ratio in THF at 25 °C afforded the corresponding bimetallic lanthanide amide complexes PARA^{Me}-{ $Ln[N(SiMe_3)_2]_2$ } (Ln = Y (1), Sm (2)) and META^{Me}-{ $Y[N(SiMe_3)_2]_2$ } (3) in 65–85% isolated yields. The similar reaction of $Ln[N(HSiMe_2)_2]_3(THF)_2$ with PARA^{Pr}-H₂ in a 2:1 molar ratio in toluene at 70 °C gave the corresponding bimetallic lanthanide amide complexes PARA^{Pr}-{ $Ln[N-(HSiMe_2)_2]_2$ } (Ln = Y (4), Sm (5)) in 72–82% isolated yields, as shown in Scheme 1.

When $L^{2,6-iPr2}_{Ph}$ -H was treated with 1 equiv. of $Y[N(TMS)_2]_3$ -(μ -Cl)Li(THF)₃ in THF at 25 °C and $Y[N(HSiMe_2)_2]_3(THF)_2$ in toluene at 70 °C, the corresponding monomeric ytrium amide complexes $L^{2,6-iPr2}_{Ph}$ - $Y[N(SiMe_3)_2]_2$ (6) and $L^{2,6-iPr2}_{Ph}$ - $Y[N(HSi-Me_2)_2(THF)]_2$ (7) were obtained in 67% and 78% isolated yields, respectively, as shown in Scheme 1.

Elemental analysis, NMR spectroscopy and X-ray crystallography confirmed the compositions of complexes 1-5, and showed that complexes 1-5 are neutral, bimetallic and solventfree species, whereas complexes 6 and 7 are monomeric species. Strong absorptions near 1550 and 1530 cm⁻¹ in the FT-IR spectra showed the delocalization of the C=N double bond in the β -diketiminate backbone.⁷ In the ¹H NMR spectra of complexes 1 and 3 (Fig. S1 and S2, ESI⁺), the signal of the NH protons of the phenylene bridged $bis(\beta$ -diketiminate) compounds at about δ 13.0 ppm disappeared, and there was only one singlet peak for the protons of the amide groups in the high-field region (near δ 0.30 ppm), suggesting a high fluxional of the amide groups in solution at room temperature. In the case of complex 4, the ¹H NMR spectrum exhibited a doublet at δ 0.12, 0.22 ppm and a singlet at 4.79 ppm with the integration of 48 H and 8 H, respectively (Fig. S3, ESI⁺), which could be assigned to the methyl protons and the Si-H protons of the -N(HSiMe₂)₂ groups, respectively, in the bimetallic yttrium complex PARA-{ $Y[N(HSiMe_2)_2]_2$ }.



Scheme 1 The synthesis of complexes 1-7.

All of these complexes are thermally stable at ambient temperature in an argon atmosphere, and are soluble in THF and toluene, but sparingly soluble in aliphatic solvents such as hexane and pentane. The single-crystal structures of complexes 1-4, 6 and 7 were determined by X-ray diffraction. Complexes 1-4 bear similar molecular structures, and they have a completely symmetric bimetallic structure, which is similar to that of the previously reported complex 9 (Chart 1).^{5h} Thus, only the molecular structure of complex 2 is provided in Fig. 1. The variation of the substitution and position on the ligand backbone showed little influence on the Ln-N (amide) σ-bond distances (the average values are 2.235(3) Å for 1 and 2.239(2) Å for 3). Meanwhile, the backbone of the β -diketiminate unit (NC3N) and the lanthanide atom form a stable six-membered ring in a boat conformation, and the C3 and lanthanide atoms are 0.19 and 1.29 Å for 1 and 0.24 and 1.49 Å for 3 out of the plane defined by N1-C2-C4-N2, respectively. The distances between the two lanthanide atoms are 9.19 Å for 1 and 8.35 Å for 3, which are somewhat longer than that of 8.10 Å in PBDI^{Me}-[Y(CH₂SiMe₃)₂]₂(THF)₂.⁶ However, the distance of Y1-Y2 in complex 4 is 7.85 Å, which is obviously shorter than that of 9.22 Å in complex 9 (Chart 1), and this might be attributed to the less sterically demanding substituents of the amide groups in complex 4.

The structure determination revealed that complexes 6 and 7 are desired monomeric β -diketiminate yttrium bis(amide) complexes. The ORTEP diagram of complex 7 is shown in Fig. 2. The structural difference in the two complexes is that



Chart 1 The molecular structure of complex 9.



Fig. 1 The ORTEP diagram of complex **2** showing an atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level and the hydrogen atoms are omitted for clarity.



Fig. 2 The ORTEP diagram of complex **7** showing an atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level and the hydrogen atoms are omitted for clarity.

there is a ligated THF molecule in complex 7, which is due to the less steric demanding nature of the N(HSiMe₂)₂ group compared with the N(SiMe₃)₂ group. The Y–N bond lengths in complexes **6** and **7** are comparable with the corresponding bond lengths in complexes **1**, **3** and **4**, and in the monomeric β -diketiminate lanthanide amides, when the difference in the ionic radii is considered.⁸

Isoprene polymerization

To test the polymerization activity of these bimetallic lanthanide amide complexes, they were employed as cationic catalyst precursors in isoprene polymerization. These neutral bimetallic lanthanide amide complexes alone showed no activity toward isoprene polymerization, and neither did the binary catalytic systems formed from complexes 1-5/AlⁱBu₃ and from complexes 1-5/[Ph₃C][B(C₆F₅)₄].⁹ However, in the presence of excess AlⁱBu₃ and on activation with 1 equiv. of [Ph₃C]- $[B(C_6F_5)_4]$ to form the ternary catalyst system, they became active for the 1,4-selective polymerization of isoprene in toluene at room temperature. The results are summarized in Table 5. It was found that the ancillary ligand had a significant effect on the polymerization activity. The complexes bearing the PARA^{Me} ligand exhibited a higher activity compared with those supported by the $PARA^{Pr}$ and $META^{Me}$ ligand. For example, complex 1 achieved complete polymerization within 5 min (Table 5, entry 2), while complexes 3 and 9 only reached 28% and 34% yields even at a prolonged polymerization time (Table 5, entries 6 and 26), indicating that the more crowded metal center hindered the orientation and insertion of the incoming monomer after the incorporation of one isoprene molecule.¹⁰ On the other hand, the polymerization activity was also dependent on the central metal. The observed activity order for the bimetallic lanthanide amido complexes was, complex 1 (Y) > complex 2 (Sm), complex 4 (Y) > complex 5 (Sm) (Table 5, entries 2 vs. 3, and 11 vs. 13), which might be

attributed to the more Lewis acidic nature of the small radius lanthanide ions.¹¹ When AlMe₃ was used instead of AlⁱBu₃, the polymerization activity decreased dramatically (Table 5, entries 7-8 vs. 10-11, and 18 vs. 22). Notably, when using the catalyst system of complex 4/AlⁱBu₃/[Ph₃C][B(C₆F₅)₄], the increase of isoprene to yttrium molar ratios from 500 to 3000 resulted in a proportional increase of the molecular weights from 37.4 to 105.6×10^4 (M_n), while the molecular weight distributions kept nearly constant $(M_w/M_n = 1.80-1.86)$ (Table 5, entries 9-12, Fig. S11, ESI[†]), suggesting a controllable polymerization nature. Additionally, compared with the binuclear β-diketiminato yttrium system PBDI^{Me}-[Y(CH₂SiMe₃)₂]₂(THF)₂/AlⁱBu₃/ $[Ph_3C][B(C_6F_5)_4]$, ⁶ $3/Al^iBu_3/[Ph_3C][B(C_6F_5)_4]$ displayed a comparable activity, but it gave the resultant polymer with a higher 1,4-regularity (88.4%) (Table 5, entry 4). The GPC curves indicated that all of the polymer samples produced by the ternary catalyst systems were unimodal, which is indicative of a singlesite polymerization behavior. This is the first example with respect to isoprene polymerization using bimetallic lanthanide amide complexes supported by β-diketiminate ligands as catalyst precursors upon to date.

To reveal whether these bimetallic lanthanide amide complexes would exhibit a cooperative effect, the corresponding monomeric counterparts **6** and **7** were also employed in isoprene polymerization for comparison. Unfortunately, under the same polymerization conditions, no obvious difference was observed in both the activity and selectivity using the monomeric and bimetallic catalyst precursors (Table 5, entries 9–12 *vs.* 17–20, 14–15 *vs.* 25–26). This may be attributed to the fact that the distances of the two metals in the above bimetallic complexes is out of the range where the two metals could interact with each other.²ⁿ

Different to the catalyst systems of the lanthanide alkyl complex/AlⁱBu₃/[Ph₃C][B(C₆F₅)₄], in which the addition sequence of $[Ph_3C][B(C_6F_5)_4]$ and Al^iBu_3 first to the lanthanide complex showed hardly any effect on the polymerization behavior, the addition sequence would affect the polymerization behavior of the lanthanide amide complexes with different amide groups. For example, no obvious influence was observed when $[Ph_3C][B(C_6F_5)_4]$ was added first, and then Al^iBu_3 , or in the reverse order using complex $L^{2,6-iPr2}_{Ph}-Y[N(SiMe_3)_2]_2$ (6) as a pre-catalyst (Table 5, entries 15 and 16). In contrast, the polymerization completed in 3 min for complex L^{2,6-iPr2}_{Ph}-Y[N- $(HSiMe_2)_2(THF)]_2$ (7) when Al^iBu_3 was added first, and then $[Ph_{3}C][B(C_{6}F_{5})_{4}];$ whereas the yield decreased dramatically when $[Ph_3C][B(C_6F_5)_4]$ was added first, and then Al^iBu_3 (Table 5, entries 19 and 21). The NMR monitoring reaction of complex 6 with 1 equiv. of $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzened₅ revealed that the reaction hardly took place even when the reaction time was prolonged to 7 days, whereas the reaction of complex 7 with 1 equiv. of $[Ph_3C][B(C_6F_5)_4]$ took place smoothly in a short time under the same conditions (Fig. S12 and S13, ESI[†]). These results revealed that the steric bulkiness of the amido groups has a profound effect on the reactivity of the corresponding β -diketiminate lanthanide amides. We postulated that the different reactivities of the amide groups with

borate resulted in the influence of the addition sequence of aluminum alkyl and borate on the polymerization.

Active species

In order to understand the essential role of the lanthanide amide complexes, and to gain some information about the active species in this polymerization, the reaction between complex 7 and AlMe3 was carried out. The treatment of complex 7 with excess AlMe₃ in hexane at room temperature, after workup, afforded the mono-diketiminate-ligated Y/Al heterodimetallic methyl complex $[L^{2,6-iPr2}_{Ph}]Y[(\mu-Me)_2AlMe_2]_2$ (8) in a 60% isolated yield, as shown in Scheme 2. The generation of complex 8 is subjected to the amide-alkyl exchange as reported previously (Fig. 3).¹² Remarkably, the NMR monitoring reaction of complex 8 with 1 equiv. of $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene-d₅ revealed that the reaction took place immediately (Scheme 3). In the ¹H NMR spectrum, the resonances of the methyl proton of the Al₂Me₈ ligand at δ -0.15 ppm disappeared (Fig. S6, ESI[†]). Instead, three singlets appeared at δ 2.10, -0.26 and -0.49 ppm with the integration of 3H, 9 H and 12 H, which could be assigned to the methyl protons of the newly generated Ph_3CMe , $AlMe_3$ and $[L^{2,6-iPr2}_{Ph}]$ - $Y[(\mu-Me)_2AlMe_2][B(C_6F_5)_4]$, respectively (Fig. 4). The new signals for the β -diketiminate ligand appeared shifted to a slightly higher field in accordance with a stronger coordination toward the highly electron-deficient rare-earth-metal cation.¹³ These



Scheme 2 The formation of complex **8**.



Fig. 3 The ORTEP diagram of complex 8 showing an atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level and the hydrogen atoms are omitted for clarity.

Paper



Scheme 3 The NMR scale reaction of complex **8** with 1 equiv. of $[Ph_3C][[B(C_6F_5)]]$ (400 MHz, $C_6D_5CI + C_6D_6$).



Fig. 4 The ¹H NMR spectrum of the reaction of complex 8 with 1 equiv. of $[Ph_3C][[B(C_6F_5)_4], 25 \circ C, after 30 min (400 MHz, C_6D_5CI + C_6D_6).$

results indicated that the combination of complex 8 with $[Ph_3C][B(C_6F_5)_4]$ resulted in the formation of the cationic β -diketiminate heterodinuclear Ln/Al species, which should be the true active species for the isoprene polymerization. 14

Conclusions

In summary, a series of bimetallic and monomeric lanthanide amide complexes stabilized by β -diketiminate ligands were prepared and well-characterized. In the presence of excess AlR₃ and on activation with 1 equiv. of [Ph₃C][B(C₆F₅)₄], all these complexes could catalyze the 1,4-selective polymerization of isoprene with a high activity in toluene at room temperature. Although a cooperative effect was not observed under the present polymerization conditions, the polymerization activity was found to be dependent on the ancillary ligand and central metal. The amide–alkyl exchange of the lanthanide amide complex with AlMe₃ occurred to give the mono-diketiminateligated Ln/Al heterodimetallic methyl complex. This heterodimetallic complex was ready to be converted into the corresponding cationic β -diketiminate Ln/Al methyl species, which was the true active species in the isoprene polymerization.

Experimental section

General procedures

All manipulations were performed in a pure argon atmosphere with the rigorous exclusion of air and moisture using standard Schlenk techniques and an argon-filled glove box. The solvents (toluene, hexane and THF) were distilled from sodium/benzo-phenone ketyl, degassed by the freeze-pump-thaw method and dried over fresh Na chips in the glove box. Anhydrous $LnCl_3$ and $[Ph_3C][B(C_6F_5)_4]$ were purchased from STREM. AlMe₃, AlⁱBu₃ and *n*-BuLi (2.5 M in a hexane solution) were purchased from Acros and used as received. Isoprene was purchased from Acros, dried by stirring with CaH₂ and distilled before polymerization. The deuterated solvents (CDCl₃, chlorobenzene-d₅, C₆D₆) were obtained from CIL. The ligands $PARA^{Pr}-H_2 = [2,6-^iPr_2C_6H_3NHC(Me)C(H)C(Me)N]_2-(para-$

phenylene),⁴ PARA^{Me}-H₂ = $[2,6^{-i}Pr_2C_6H_3NHC(Me)C(H)C(Me)N]_2$ -(*para*-phenylene),⁴ META^{Me}-H₂ = $[2,6^{-i}Pr_2C_6H_3NHC(Me)C(H)-C(Me)N]_2$ -(*meta*-phenylene),⁴ L^{2,6-2iPr2}_{Ph} = $(2,6^{-i}Pr_2C_6H_3)NHC$ -(Me)CHC(Me)N(C₆H₅),^{15a} Ln[N(TMS)₂]₃(µ-Cl)Li(THF)₃ (Ln = Sm, Y)^{15b} and Ln[N(HSiMe_2)_2]_3(THF)_2 (Ln = Sm, Y)^{15c} were prepared according to the literature.

Samples of the organolanthanide complexes for the NMR spectroscopic measurements were prepared in the glove box using *J. Young* valve NMR tubes. The NMR (¹H, ¹³C) spectra were recorded on a Varian Unity spectrometer at 25 °C. The carbon, hydrogen and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The FT-IR spectra were recorded with a Nicolet-550 FT-IR spectrometer as KBr pellets. The molecular weight and molecular weight distribution were determined against polystyrene standards by gel permeation chromatography (GPC) on a PL 50 apparatus and THF was used as an eluent at a flow rate of 1.0 mL min⁻¹ at 40 °C.

PARA^{Me}-{**Y**[**N**(SiMe₃)₂]₂}₂ (1). A THF solution of Y[N(TMS)₂]₃- $(\mu$ -Cl)Li(THF)₃ (3.31 g, 4.00 mmol) was added dropwise into a THF solution of PARA^{Me}-H₂ (0.96 g, 2.00 mmol) at room temperature. The mixture was stirred at 25 °C overnight, and then THF was evaporated completely under reduced pressure. Toluene (35 mL) was added to the residue, and the mixture was stirred at 80 °C for about 12 h. After the precipitate was removed by centrifugation, the resulting filtrate was dried completely under reduced pressure. Colorless crystals were obtained from concentrated toluene solution (about 13 mL) at 25 °C in a few days (1.89 g, 73%). Mp: 259-261 °C. ¹H NMR (C₆D₆, 300 MHz): 7.24 (d, 4H, CH_{N-arvl}), 6.96 (s, 6H, CH_{N-arvl}), 5.12 (s, 2H, CH₃CNCH), 3.10 (m, 4H, CH(CH₃)₂), 2.23 (s, 12H, Ar-CH₃), 1.86 (s, 6H, CH₃CN), 1.50 (s, 6H, CH₃CN), 0.29 (s, 72H, TMS). ¹³C NMR (75 MHz, C₆D₆): δ 4.7 (Si(CH₃)₃), 19.6 (Ar-CH₃), 23.6 (CH₃CN), 24.9 (CH₃CN), 97.9 (CH₃CNCH), 125.2 (CH_{N-aryl}), 126.8 (CH_{N-aryl}), 128.9 (CH_{Naryl}), 131.5 (CH_{Naryl}), 146.0 (C=N), 147.2 (C=N), 165.5 (C=N), 167.4 (C=N). FT-IR (KBr, cm^{-1}): 3053 (s), 3029 (s), 2961 (s), 2869 (m), 1625 (s), 1552 (s), 1515 (s), 1459 (s), 1435 (s), 1380 (s), 1368 (s), 1280 (m), 1165 (m), 998 (w), 887 (s), 840 (s), 756 (m). Anal. calcd for C₅₆H₁₀₈N₈Si₈Y₂: C, 51.90; H, 8.40; N, 8.65. Found: C, 51.81; H, 8.56; N, 8.69.

PARA^{Me}-{Sm[N(SiMe₃)₂]₂} (2). The synthesis of complex 2 was carried out in the same way as that described for complex 1, but Sm[N(TMS)₂]₃(µ-Cl)Li(THF)₃ (3.56 g, 4.00 mmol) was used instead of Y[N(TMS)₂]₃(µ-Cl)Li(THF)₃. Yellow crystals were obtained from a concentrated toluene solution (about 15 mL) at 25 °C in a few days (1.96 g, 69%). Mp: 271–273 °C. FT-IR (KBr, cm⁻¹): 3060 (m), 2963 (s), 2892 (m), 2873 (s), 1625 (s), 1554 (s), 1510 (s), 1460 (s), 1435 (s), 1385 (s), 1360 (m), 1274 (m), 1256 (m), 1181 (w), 942 (s), 887 (s), 751 (m). Anal. calcd for $C_{56}H_{108}N_8Si_8Sm_2$: C, 47.40; H, 7.67; N, 7.90. Found: C, 47.51; H, 7.73; N, 8.03.

META^{Me}-{Y[N(SiMe₃)₂]₂}₂ (3). The synthesis of complex 3 was carried out in the same way as that described for complex 1, but META^{Me}-H₂ (0.96 g, 2.00 mmol) was used instead of PARA^{Me}-H₂. Colorless crystals were obtained from a

concentrated toluene solution (about 20 mL) at 25 °C in a few days (1.68 g, 65%). Mp: 228–231 °C. ¹H NMR (C_6D_6 , 400 MHz): 7.16 (d, 4H, CH_{N-aryl}), 6.97 (m, 6H, CH_{N-aryl}), 6.51 (s, 1H, CH_{N-aryl}), 5.13 (s, 2H, CH_3CNCH), 2.25 (s, 12H, Ar- CH_3), 1.89 (s, 6H, CH_3CN), 1.53 (s, 6H, CH_3CN), 0.30 (s, 72H, TMS). ¹³C NMR (100 MHz, C_6D_6): δ 5.0 (Si(CH_3)₃), 20.0 (Ar- CH_3), 23.9 (CH_3CN), 25.6 (CH_3CN), 97.4 (CH_3CNCH), 122.5 (CH_{N-aryl}), 123.2 (CH_{N-aryl}), 125.5 (CH_{Naryl}), 129.1 (CH_{Naryl}), 131.4 (CH_{Naryl}), 147.1 (CH_{Naryl}), 147.4 (C=N), 150.8 (C=N), 165.4 (C=N), 167.3 (C=N). FT-IR (KBr, cm⁻¹): 3056 (s), 3030 (s), 2960 (s), 2868 (m), 1625 (s), 1552 (s), 1515 (s), 1459 (s), 1430 (s), 1382 (s), 1371 (s), 1282 (m), 1168 (m), 986 (w), 881 (s), 848 (s), 753 (m). Anal. calcd for $C_{56}H_{108}N_8Si_8Y_2$: C, 51.90; H, 8.40; N, 8.65. Found: C, 51.83; H, 8.61; N, 8.72.

PARA^{Pr}-{**Y**[**N**(**HSiMe**₂)₂]₂}₂ (4). A toluene solution of Y[N(HSi- $Me_2_2_3$ (THF)₂ (1.25 g, 2.00 mmol) was added dropwise into a toluene solution of PARA^{Pr}-H₂ (10 mL, 0.59 g, 1.00 mmol). The mixture was stirred overnight at 70 °C. The removal of the volatiles under vacuum produced a light vellow powder. The resulting powder was dissolved in about 10 mL of hexane, and a small amount of the precipitate formed was removed by centrifugation. The solution was kept at room temperature overnight to give complex 4 as yellow crystals (1.06 g, 82%). Mp: 213-215 °C. ¹H NMR (C₆D₆, 300 MHz): 7.31 (s, 4H, CH_{N-aryl}), 7.09 (s, 6H, CH_{N-arvl}), 5.19 (s, 2H, CH₃CNCH), 4.84 (s, 8H, SiHMe₂), 3.13 (m, 4H, CH(CH₃)₂), 2.04 (s, 6H, CH₃CN), 1.65 (s, 6H, CH₃CN), 1.33 (d, 12H, CH(CH₃)₂), 1.15 (d, 12H, CH(CH₃)₂), 0.17 (d, 48H, SiHMe₂). ¹³C NMR (75 MHz, C₆D₆): δ 2.7 (SiHMe₂), 23.7 (CH₃CN), 23.8 (CH₃CN), 24.1 (CH(CH₃)₂), 24.2 $(CH(CH_3)_2)$, 28.6 $(CH(CH_3)_2)$, 93.9 (CH_3CNCH) , 98.5 (CH₃CNCH), 124.0 (CH_{N-arvl}), 125.7 (CH_{N-arvl}), 126.1 (CH_{Narvl}), 123.8 (CH_{Naryl}), 126.2 (CH_{Naryl}), 127.0 (CH_{Naryl}), 141.9 (CH_{N-arvl}), 143.1 (C=N), 144.1 (C=N), 163.6 (C=N), 167.8 (C=N). FT-IR (KBr, cm⁻¹): 3057 (s), 2960 (s), 2867 (m), 2110 (m), 2069 (m), 1625 (s), 1552 (s), 1508 (s), 1461 (s), 1435 (s), 1380 (s), 1363 (s), 1325 (m), 1276 (s), 1177 (s), 1100 (w), 855 (s), 787 (m), 757 (m). Anal. calcd for C₅₆H₁₀₈N₈Si₈Y₂: C, 51.90; H, 8.40; N, 8.65. Found: C, 51.85; H, 8.53; N, 8.72.

PARA^{Pr}-{**Sm**[**N**(**HSiMe**₂)₂]₂}₂ (5). The synthesis of complex 5 was carried out in the same way as that described for complex 4, but $\text{Sm}[\text{N}(\text{HSiMe}_2)_2]_3(\text{THF})_2$ (1.38 g, 2.00 mmol) was used instead of $\text{Y}[\text{N}(\text{HSiMe}_2)_2]_3(\text{THF})_2$. Yellow crystals were obtained from a concentrated toluene solution (about 8 mL) at 25 °C in a few days (1.15 g, 81%). Mp: 203–205 °C. FT-IR (KBr, cm⁻¹): 3060 (m), 2960 (s), 2867 (m), 2111 (m), 2068 (m), 1626 (s), 1552 (s), 1508 (s), 1460 (s), 1435 (s), 1380 (s), 1365 (m), 1276 (s), 1257 (s), 1177 (s), 1100 (s), 1026 (m), 934 (s), 789 (s), 757 (m). Anal. calcd for C₅₆H₁₀₈N₈Si₈Sm₂: C, 47.40; H, 7.67; N, 7.90. Found: C, 47.46; H, 7.81; N, 7.83.

 $L^{2,6-iPr2}_{Ph}$ **Y**[**N**(**SiMe**₃)₂]₂ (6). The synthesis of complex 6 was carried out in the same way as that described for complex 1, but $L^{2,6-iPr2}_{Ph}$ -H (1.34 g, 4.00 mmol) was used instead of PARA^{Me}-H₂. Colorless crystals were obtained from a concentrated hexane solution (about 6 mL) at 25 °C in a few days (1.99 g, 67%). Mp: 187–190 °C. ¹H NMR (C_6D_6 , 300 MHz): 7.19 (m, 3H, CH_{N-arvl}), 7.09 (s, 4H, CH_{N-arvl}), 6.98 (t, 3H, CH_{N-arvl}),

5.10 (s, 1H, CH₃CNCH), 3.10 (m, 2H, CH(CH₃)₂), 1.80 (s, 3H, CH₃CN), 1.67 (s, 3H, CH₃CN), 1.34 (d, 6H, CH(CH₃)₂), 1.10 (d, 6H, CH(CH₃)₂), 0.29 (s, 36H, TMS). ¹³C NMR (75 MHz, C₆D₆): δ 5.17 (Si(CH₃)₃), 24.90 (CH₃CN), 25.28 (CH(CH₃)₂), 25.82 (CH(CH₃)₂), 97.64 (CH₃CNCH), 124.53 (CH_{N-aryl}), 124.94 (CH_{N-aryl}), 125.66 (CH_{Naryl}), 126.23 (CH_{Naryl}), 128.92 (CH_{Naryl}), 142.02 (C=N), 145.51 (C=N), 149.79 (C=N), 164.74 (C=N), 167.67 (C=N). IR (KBr, cm⁻¹): 3058 (m), 3029 (s), 2960 (s), 2866 (m), 1624 (s), 1596 (m), 1555 (m), 1504 (m), 1485 (s), 1437 (m), 1381 (s), 1363 (s), 1282 (m), 1102 (m), 1177 (s), 1028 (w), 933 (m), 840 (s), 760 (s). Anal. calcd for C₃₅H₆₅N₄Si₄Y: C, 56.57; H, 8.82; N, 7.54. Found: C, 56.68; H, 8.93; N, 7.63.

 $L^{2,6-iPr2}_{Ph}Y[N(HSiMe_2)_2]_2$ (7). The synthesis of complex 7 was carried out in the same way as that described for complex 4, but L^{2,6-2iPr2}_{Ph}-H (0.67 g, 2.00 mmol) was used instead of PARA-H₂. Colorless crystals were obtained from a concentrated hexane solution (about 4 mL) at 25 °C in a few days (1.07 g, 78%). Mp: 179-181 °C. ¹H NMR (C₆D₆, 300 MHz): 7.21 (m, 4H, CH_{N-aryl}), 7.09 (s, 3H, CH_{N-aryl}), 6.98 (m, 1H, CH_{N-aryl}), 5.14 (s, 1H, CH₃CNCH), 4.82 (m, 4H, SiHMe₂), 3.12 (m, 2H, CH(CH₃)₂), 1.85 (s, 3H, CH₃CN), 1.64 (s, 3H, CH₃CN), 1.34 (d, 6H, $CH(CH_3)_2$, 1.14 (d, 6H, $CH(CH_3)_2$), 0.12 (d, 24H, $SiHMe_2$). ¹³C NMR (100 MHz, C₆D₆): δ 2.9 (Si(CH₃)₃), 23.6 (CH₃CN), 24.1 (CH₃CN), 24.4 (CH(CH₃)₂), 24.5 (CH(CH₃)₂), 28.8 (CH(CH₃)₂), 98.6 (CH₃CNCH), 124.3 (CH_{N-aryl}), 124.8 (CH_{N-aryl}), 124.9 (CH_{Naryl}), 126.4 (CH_{Naryl}), 129.8 (CH_{Naryl}), 142.3 (CH_{Naryl}), 143.3 (C=N), 147.4 (C=N), 163.7 (C=N), 168.1 (C=N). FT-IR (KBr, cm⁻¹): 3059 (s), 2960 (s), 2870 (m), 2109 (m), 2072 (m), 1625 (s), 1552 (s), 1510 (s), 1462 (s), 1438 (s), 1381 (s), 1365 (s), 1328 (m), 1275 (s), 1177 (s), 1100 (w), 855 (s), 786 (m), 753 (m).

Anal. calcd for C₃₁H₅₇N₄Si₄Y: C, 54.19; H, 8.36; N, 8.15. Found: C, 54.23; H, 8.41; N, 8.26 (coordinated THF was removed under vacuum).

 $L^{2,6-iPr2}_{Ph}Y[(\mu-Me)_2AlMe_2]_2$ (8). A hexane (5 mL) solution of complex 7 (0.34 g, 0.5 mmol) was added dropwise to a heptane solution (3 mL) of AlMe₃ (3 mmol, 1.0 M) at room temperature. The reaction mixture was stirred at room temperature overnight to give a pale white solution with a large amount of precipitate. The removal of the volatiles under vacuum produced a pale white powder. The resulting pale white powder was dissolved in about 6 mL of a hexane-toluene (4/2, v/v) mixture and was kept at -30 °C overnight to give complex 8 as colorless crystals (0.18 g, 60%). Mp: 235–238 °C. $^1\mathrm{H}$ NMR (C_6D_6, 400 MHz): 7.24 (m, 4H, CH_{N-aryl}), 7.12 (m, 3H, CH_{N-aryl}), 7.06 (m, 1H, CH_{N-aryl}), 5.21 (s, 1H, CH₃CNCH), 3.13 (m, 2H, CH(CH₃)₂), 1.71 (s, 3H, CH₃CN), 1.64 (s, 3H, CH₃CN), 1.37 (d, 6H, $CH(CH_3)_2$, 1.06 (d, 6H, $CH(CH_3)_2$), -0.08 (s, 24H, $[AlMe_4]^-$). ¹³C NMR (100 MHz, C₆D₆): δ 1.4 ($[AlMe_4]^-$), 23.8 (CH₃CN), 25.0 (CH(CH₃)₂), 25.1 (CH(CH₃)₂), 26.0 (CH(CH₃)₂), 28.7 (CH(CH₃)₂), 100.7 (CH₃CNCH), 125.4 (CH_{N-arvl}), 126.1 (CH_{N-aryl}), 126.6 (CH_{Naryl}), 127.6 (CH_{Naryl}), 129.6 (CH_{Naryl}), 142.5 (CH_{Naryl}), 143.0 (C=N), 149.3 (C=N), 166.7 (C=N), 169.7 (C=N). Anal. calcd for C₃₁H₅₃Al₂N₂Y: C, 62.41; H, 8.95; N, 4.70. Found: C, 62.50; H, 8.90; N, 4.75.

The typical procedure for the isoprene polymerization

The procedures for the isoprene polymerization catalyzed by these lanthanide amides were similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask equipped with a magnetic stirring bar was charged in

Compound	1	2	3	4		
Formula	$C_{56}H_{108}N_8Si_8Y_2$	$C_{56}H_{108}N_8Si_8Sm_2$	$C_{56}H_{108}N_8Si_8Y_2$	$C_{56}H_{108}N_8Si_8Y_2$		
fw	1296.04	1418.92	1296.04	1296.04		
T/K	223(2) K	223(2) K	220(2)	293(2)		
Crystal system	Triclinic	Triclinic	Orthorhombic	Monoclinic		
Crystal size/mm	0.60 imes 0.40 imes 0.20	$0.50 \times 0.18 \times 0.12$	0.75 imes 0.66 imes 0.50	0.55 imes 0.35 imes 0.10		
Space group	$P\bar{1}$	$P\bar{1}$	C2221	C2/c		
a/Å	11.1103(18)	11.2006(12)	16.9447(7)	10.5762(8)		
b/Å	11.4141(19)	11.4482(11)	18.8097(9)	20.4287(10)		
c/Å	15.307(2)	15.2323(13)	23.3593(11)	34.9745(18)		
$\alpha / ^{\circ}$	92.761(4)	92.946(2)				
$\beta / ^{\circ}$	92.247(3)	93.603(2)		95.853(6)		
$\gamma/^{\circ}$	108.104(4)	108.289(3)				
$V/Å^3$	1839.9(5)	1845.6(3)	7445.2(6)	7517.1(8)		
Ζ	1	1	4	4		
$D_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.170	1.277	1.156	1.145		
μ/mm^{-1}	1.736	1.742	1.716	1.700		
F(000)	690	736	2760	2760		
$\theta_{\rm max}/^{\circ}$	25.50	25.50	25.50	25.50		
Collected	14 910	15 907	23 492	19 022		
Unique reflns	6792	6812	6861	6980		
Obsd reflns $[I > 2.0\sigma(I)]$	4974	6104	5924	4464		
No. of variables	351	351	351	300		
GOF	1.044	1.041	1.030	1.049		
R	0.0473	0.0316	0.0348	0.0843		
wR	0.1144	0.0619	0.0698	0.2142		
R _{int}	0.0411	0.0372	0.0463	0.0678		
Largest diff. peak, hole/e $Å^{-3}$	0.703, -0.578	0.731, -0.541	0.528, -0.342	1.587, -2.061		

Table 1 The crystallographic data for complexes 1 /

Table 2 The crystallographic data for complexes 6-8

Compound	6	7	8
Formula	C35H65N4Si4Y	C35H65N4OSi4Y	C ₃₁ H ₅₃ Al ₂ N ₂ Y
fw	743.18	759.18	596.62
T/K	223(2) K	293(2)	293(2)
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Crystal size/mm	0.60 imes 0.40 imes	0.75 imes 0.60 imes	0.80 imes 0.70 imes
·	0.20	0.20	0.40
Space group	Pbca	$Pca2_1$	$P121/n_{1}$
a/Å	20.0835(9)	18.189(2)	12.6433(12)
b/Å	20.5924(12)	14.5123(12)	20.8974(18)
c/Å	20.6268(10)	16.414(5)	13.2484(13)
$\alpha/^{\circ}$			
β / \circ			98.252(3)
$\gamma/^{\circ}$			
$V/\text{\AA}^3$	8530.6(8)	4332.8(15)	3464.1(6)
Ζ	8	4	4
$D_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.157	1.164	1.144
μ/mm^{-1}	1.506	1.486	1.754
F(000)	3184	1624	1272
$\theta_{\rm max}/^{\rm o}$	25.50	26.39	25.35
Collected	25 980	24 412	33 231
Unique reflns	7897	8388	6331
Obsd reflns	5961	6598	5521
$[I > 2.0\sigma(I)]$			
No. of variables	416	396	384
GOF	1.170	1.007	1.070
R	0.0767	0.0470	0.0578
wR	0.1245	0.1033	0.1320
$R_{\rm int}$	0.0738	0.0490	0.0510
Largest diff. peak, hole/e Å ⁻³	0.253, -0.411	0.554, -0.349	0.431, -0.420

Table 3 The selected bond lengths (Å) and bond angles (°) for complexes 1-4

Bond lengths	1	2	3	4
Ln1-N1	2.303(3)	2.272(2)	2.298(2)	2.317(6)
Ln1-N2	2.383(3)	2.300(2)	2.365(2)	2.298(6)
Ln1-N3	2.222(3)	2.375(3)	2.232(2)	2.236(6)
Ln1-N4	2.249(3)	2.436(3)	2.246(2)	2.239(6)
Bond angles				
N3-Ln1-N4	110.09(11)	110.45(9)	109.47(9)	116.6(2)
N3-Ln1-N1	123.31(11)	128.31(9)	123.27(9)	113.2(2)
N4-Ln1-N1	103.72(11)	104.65(9)	103.93(9)	121.9(2)
N3-Ln1-N2	97.04(11)	96.03(9)	100.31(9)	114.5(2)
N4-Ln1-N2	143.93(10)	142.53(9)	140.05(9)	103.9(2)

sequence with the desired amount of the lanthanide amide, toluene, borate (or triisobutylaluminum and borate) and isoprene. The mixture was stirred vigorously at room temperature for the desired time, during which an increase of viscosity was observed. The reaction mixture was quenched by the addition of ethanol and then poured into a large amount of ethanol to precipitate the polymer, which was dried under vacuum at 60 °C and weighed.

X-Ray crystallographic structure determinations

Suitable single crystals of complexes **1–4** and **6–8** were sealed in a thin-walled glass capillary to determine the single-crystal structures. The intensity data were collected with a Rigaku Mercury CCD area detector in the ω scan mode using Mo K α radiation ($\lambda = 0.71070$ Å). The diffracted intensities were corrected for Lorentz/polarization effects and empirical absorption corrections. The details of the intensity data collection and crystal data are given in Tables 1 and 2.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of the full-matrix leastsquares refinement. The structures were solved and refined using the *SHELEXL-97* program. The selected bond parameters are summarized in Tables 3 and 4.

Acknowledgements

Financial support from the National Natural Science Foundation of China (grants 21174095, 21172195, and 21132002), PAPD, and the Qing Lan Project is gratefully acknowledged.

Table 4 The selected	bond lengths (Å) and bond a	angles (°) for complexes 6–8			
Bond lengths	6	Bond lengths	7	Bond lengths	8
Ln1-N1	2.323(4)	Ln1–N1	2.370(3)	Ln1–N1	2.339(3)
Ln1-N2	2.352(3)	Ln1–N2	2.349(3)	Ln1–N2	2.277(3)
Ln1-N3	2.255(3)	Ln1–N3	2.275(4)	Ln1–C24	2.548(5)
Ln1-N4	2.225(3)	Ln1–N4	2.253(4)	Ln1–C25	2.573(5)
		Ln1–O1	2.425(3)	Al1–C26	1.960(5)
				Al1-C27	1.966(5)
Bond angles		Bond angles		Bond angles	
N4-Ln1-N3	110.09(13)	N3-Ln1-N4	124.45(17)	N1-Ln1-N2	80.66(10)
N4-Ln1-N1	121.65(13)	N3-Ln1-N1	105.83(13)	C24-Ln1-C25	82.31(17)
N3-Ln1-N1	104.76(13)	N4-Ln1-N1	101.92(13)	C24-Al1-C25	109.0(2)
N4-Ln1-N2	99.99(12)	N3-Ln1-N2	127.68(13)	C26-Al1-C27	117.6(2)
N3-Ln1-N2	139.21(13)	N4-Ln1-N2	104.60(14)		
N1-Ln1-N2	80.58(12)	N1-Ln1-N2	77.77(12)		
		N4-Y1-O1	87.66(12)		
		N3-Y1-O1	82.99(12)		
		N2-Y1-O1	81.88(11)		
		N1-Y1-O1	159.11(11)		

Paper

Table 5 The polymerization of isoprene with complexes 1–9 under activation of organic borate and trialkylaluminium⁶

Entry	Cat	[IP]/[Ln]	$[Ln]_0/[Al]_0/[Bc]_0$	Time	Yield (%)	$M_{ m n}(imes 10^4)^b$	PDI^{b}	$1,4^{c}(\%)$
1	1	1000	1/5/1	2 min	100	19.7	1.41	91.0
2	1	2000	1/5/1	5 min	100	25.1	1.79	89.3
3	2	2000	1/5/1	10 min	58	11.0	1.60	91.7
4	3	500	1/5/1	5 min	100	12.7	1.53	88.4
5	3	1000	1/5/1	2 min	40	19.7	1.41	87.7
6	3	2000	1/5/1	10 min	28	24.2	1.99	87.7
7^d	4	1000	1/5/1	1 h	53	79.1	1.65	91.7
8^d	4	2000	1/5/1	3 h	26	63.9	1.51	91.7
9	4	500	1/5/1	2 min	100	37.4	1.80	89.3
10	4	1000	1/5/1	2 min	100	47.4	1.88	89.3
11	4	2000	1/5/1	3 min	100	82.1	1.84	88.5
12	4	3000	1/5/1	2 min	100	105.6	1.86	87.7
13	5	2000	1/5/1	4 min	71	35.1	1.31	89.3
14	6	2000	1/5/1	3 min	10	36.1	1.95	92.6
15	6	2000	1/5/1	5 min	23	37.5	2.11	92.6
16^e	6	2000	1/5/1	5 min	20	37.8	2.06	90.9
17	7	500	1/5/1	2 min	100	21.8	1.87	93.4
18	7	1000	1/5/1	2 min	100	34.3	1.92	92.6
19	7	2000	1/5/1	3 min	100	69.4	1.63	91.7
20	7	3000	1/5/1	3 min	100	118.1	1.93	91.7
21^e	7	2000	1/5/1	5 min	37	55.6	1.74	91.9
22^d	7	1000	1/5/1	40 min	43	97.9	1.78	92.5
23	8	1000	1/0/1	40 min	47	99.7	1.91	93.4
24	8	1000	1/0/0	4 h	0	/	/	
25	9	2000	1/5/1	3 min	11	44.6	1.92	89.3
26	9	2000	1/5/1	10 min	34	78.7	1.93	89.3

^{*a*} Polymerization conditions: in toluene; Ln 15 μ mol; AlⁱBu₃ 75 μ mol; B_C 13.8 mg (B_C = [Ph₃C][[B(C₆F₅)₄]); 1/5 (v/v) isoprene-toluene; 25 °C. ^{*b*} Determined by GPC in THF at 40 °C against a polystyrene standard. ^{*c*} Determined by ¹H NMR in CDCl₃. ^{*d*} AlMe₃ was used instead of AlⁱBu₃. ^{*e*} The addition sequence: Ln, then B_C, last AlⁱBu₃.

Notes and references

- (a) A. L. Gavrilova and B. Bosnich, *Chem. Rev.*, 2004, **104**, 349; (b) H. Li and T. J. Marks, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15295; (c) V. Ritleng and M. J. Chetcuti, *Chem. Rev.*, 2007, **107**, 797; (d) S. Singh and H. W. Roesky, *Dalton Trans.*, 2007, 1360.
- 2 (a) D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, J. Am. Chem. Soc., 2003, 125, 11911; (b) M. J. McNevin and J. R. Hagadorn, Inorg. Chem., 2004, 43, 8547; (c) B. M. Trost, A. Fettes and B. T. Shireman, J. Am. Chem. Soc., 2004, 126, 2660; (d) S. Matsunaga, T. Yoshida, H. Morimoto, N. Kumagai and M. Shibasaki, J. Am. Chem. Soc., 2004, 126, 8777; (e) B. Y. Lee, H. Y. Kwon, S. Y. Lee, S. J. Na, S. Han, H. Yun, H. Lee and Y. W. Park, J. Am. Chem. Soc., 2005, 127, 3031; (f) Y. L. Xiao, Z. Wang and K. L. Ding, Macromolecules, 2006, 39, 128; (g) S. B. Amin and T. J. Marks, J. Am. Chem. Soc., 2007, 129, 2938; (h) B. A. Rodriguez, M. Delferro and T. J. Marks, Organometallics, 2008, 27, 2166; (i) A. Arbaoui, C. Redshaw and D. L. Hughes, Chem. Commun., 2008, 4717; (j) N. C. Guo, L. Stern and T. J. Marks, J. Am. Chem. Soc., 2008, 130, 2246; (k) A. Motta, I. L. Fragalà and T. J. Marks, J. Am. Chem. Soc., 2009, 131, 3974; (l) B. A. Rodriguez, M. Delferro and T. J. Marks, J. Am. Chem. Soc., 2009, 131, 5902; (m) A. Buchard, M. R. Kember, K. G. Sandemanb and C. K. Williams, Chem. Commun., 2011, 47, 212; (n) J. H. H. Ho, S. W. S. Choy, S. A. Macgregor and

B. A. Messerle, Organometallics, 2011, **30**, 5978; (o) M. P. Weberski, C. Chen, M. Delferro, C. Zuccaccia, A. Macchioni and T. J. Marks, Organometallics, 2012, **31**, 3773; (p) W. Y. Li, W. T. Wu, Y. R. Wang, Y. M. Yao, Y. Zhang and Q. Shen, Dalton Trans., 2011, **40**, 11378; (q) W. Y. Li, Y. M. Yao, Y. Zhang and Q. Shen, Chin. J. Chem., 2012, **30**, 609.

- 3 (a) H. Li, L. Li and T. J. Marks, Angew. Chem., Int. Ed., 2004,
 43, 4937; (b) H. Li, L. Li, D. J. Schwartz, C. L. Stern and
 T. J. Marks, J. Am. Chem. Soc., 2005, 127, 14756; (c) H. Li,
 C. L. Stern and T. J. Marks, Macromolecules, 2005, 38, 9015.
- 4 D. F. J. Piesik, S. Range and S. Harder, *Organometallics*, 2008, 27, 6178.
- 5 (a) J. F. Wang, T. Cai, Y. M. Yao, Y. Zhang and Q. Shen, Dalton Trans., 2007, 5275; (b) H. F. Yuen and Marks, Organometallics, 2008, 27, Т. I. 155: (c) Z. J. Zhang, X. P. Xu, S. Sun, Y. M. Yao, Y. Zhang and Q. Shen, Chem. Commun., 2009, 7414; (d) J. F. Wang, Y. M. Yao, Y. Zhang and Q. Shen, Inorg. Chem., 2009, 48, 744; (e) H. F. Yuen and T. J. Marks, Organometallics, 2009, 28, 2423; (f) W. Y. Li, Z. J. Zhang, Y. M. Yao, Y. Zhang and Q. Shen, Organometallics, 2012, 31, 3499; (g) S. Sun, Q. Sun, B. Zhao, Y. Zhang, Q. Shen and Y. M. Yao, Organometallics, 2013, 32, 1876; (h) S. Sun, K. Nie, Y. Tan, B. Zhao, Y. Zhang, Q. Shen and Y. Yao, Dalton Trans., 2013, 42, 2870.
- 6 L. Li, C. Wu, D. Liu, S. Li and D. Cui, Organometallics, 2013, 32, 3203.

- 7 D. S. Richeson, J. F. Mitchell and K. H. Theopold, J. Am. Chem. Soc., 1987, 109, 5868.
- 8 Y. Yao, Z. Zhang, H. Peng, Y. Zhang, Q. Shen and J. Lin, *Inorg. Chem.*, 2006, **45**, 2175.
- 9 (a) Y. J. Luo, S. M. Fan, J. P. Yang, J. H. Fang and P. Xu, *Dalton Trans.*, 2011, 40, 3053; (b) F. Chen, S. M. Fan, Yi. B. Wang, J. Chen and Y. J. Luo, *Organometallics*, 2012, 31, 3730; (c) C. Döring, W. P. Kretschmer, T. Bauer and R. Kempe, *Eur. J. Inorg. Chem.*, 2009, 4255.
- 10 (a) D. Wang, S. Li, X. Liu, W. Gao and D. Cui, Organometallics, 2008, 27, 6531; (b) W. Gao and D. M. Cui, J. Am. Chem. Soc., 2008, 130, 4984; (c) W. Rong, D. Liu, H. Zuo, Y. Pan, Z. Jian, S. Li and D. Cui, Organometallics, 2013, 32, 1166.
- 11 W. Gao and D. M. Cui, J. Am. Chem. Soc., 2008, 130, 4984.
- 12 (a) M. Zimmermann and R. Anwander, *Chem. Rev.*, 2010, 110, 6194; (b) G. Occhipinti, C. Meermann, H. M. Dietrich, R. Litlabo, F. Auras, K. W. Törnroos, C. M. Mossmer, V. R. Jensen and R. Anwander, *J. Am. Chem. Soc.*, 2011, 133, 6323; (c) H. M. Dietrich, K. W. Tornroos, E. Herdtweck and R. Anwander, *Organometallics*, 2009, 28, 6739; (d) S. Hamidi, L. N. Jende, H. M. Dietrich, C. Maichle-Mössmer, K. W. Törnroos, G. B. Deacon, P. C. Junk and R. Anwander, *Organometallics*, 2013, 32, 1209; For examples

of the formation of yttrium tetramethylaluminum complexes, see: (*e*) C. T. Carver, M. J. Monreal and P. L. Diaconescu, *Organometallics*, 2008, **27**, 363.

- 13 (a) M. Zimmermann, K. W. Tornroos and R. Anwander, Angew. Chem., Int. Ed., 2008, 47, 775; (b) R. Litlabø, M. Enders, K. W. Tornroos and R. Anwander, Organometallics, 2010, 29, 2588.
- 14 (a) L. X. Zhang, M. Nishiura, M. Yuki, Y. Luo and Z. M. Hou, Angew. Chem., Int. Ed., 2008, 47, 2642;
 (b) C. Doring, W. P. Kretschmer, T. Bauer and R. Kempe, Eur. J. Inorg. Chem., 2009, 4255; (c) J. Q. Hong, L. X. Zhang, X. Y. Yu, M. Li, Z. X. Zhang, P. Z. Zhang, M. Nishiura, Z. M. Hou and X. G. Zhou, Chem.-Eur. J., 2011, 17, 2130;
 (d) Y. J. Luo, S. M. Fan, J. P. Yang, J. H. Fang and P. Xu, Dalton Trans., 2011, 40, 3053; (e) F. Chen, S. M. Fan, Yi. B. Wang, J. Chen and Y. J. Luo, Organometallics, 2012, 31, 3730.
- 15 (a) Y. M. Yao, Y. J. Luo, R. Jiao, Q. Shen, K. B. Yu and L. H. Weng, *Polyhedron*, 2003, 22, 441; (b) S. L. Zhou, S. W. Wang, G. S. Yang, X. Y. Liu, E. H. Sheng, K. H. Zhang and L. Cheng, *Polyhedron*, 2003, 22, 1019; (c) R. Anwander, O. Runte, J. Eppinger, G. Gerstberger, E. Herdtweek and M. Spiegler, *J. Chem. Soc., Dalton Trans.*, 1998, 847.