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Rare-earth metal bis(silylamide) complexes supported by mono-dentate arylamido ligand: synthesis, reactivity, and catalyst precursors in living *cis*-1,4-selective polymerization of isoprene

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Abstract Salt metathesis reaction of $LnCl_3$ with 1 equivalent of arylamido lithium $[2,6\text{-}^i Pr_2C_6H_3N(SiMe_3)]Li$, followed by addition of 2 equivalents of $LiN(SiHMe_2)_2$ in THF at room temperature gave the neutral mono-arylamido-ligated rare-earth metal bis(silylamide) complexes $[2,6\text{-}^i Pr_2C_6H_3N(SiMe_3)]Ln[N(SiHMe_2)_2]_2(THF)$ (Ln = Y (**1**), Lu (**2**), La (**3**)) in good isolated yields. Treatment of **1-3** with excess $AlMe_3$ produced the mono(arylamido) Ln/Al heterotrinuclear methyl complexes $[2,6\text{-}^i Pr_2C_6H_3N(SiMe_3)]Ln[(\mu\text{-}Me)_2AlMe_2]_2$ (Ln = Y (**4**), Lu (**5**), La (**6**)) via amide-alkyl exchange. All these complexes were well-characterized by elemental analysis, NMR spectroscopy and FT-IR spectroscopy. **2**, **4** and **5** were further structurally authenticated by X-ray crystallography. In the presence of $[Ph_3C][B(C_6F_5)_4]$ and Al^iBu_3, **1-3** were highly active for *cis*-1,4-selective polymerization of isoprene, while **2**/$[Ph_3C][B(C_6F_5)_4]$/Al^iBu_3 promoted the polymerization in a living fashion.

Introduction

Over the past decades tremendous research efforts have been devoted to the development of organo-rare-earth metal complexes, which have been proved to be efficient catalyst precursors in organic transformation and polymerization.[1] Compared to well-established cyclopentadienyl anions (Cp ligand sets), alternative non-Cp ligand scaffolds such as β-diketiminate, amidinate, guanidinate, and phenolate are also receiving considerable attention to create different steric and electronic environments at the reactive site of rare-earth metals.[1h] Most of the non-Cp spectator ligands are bounded to central metals through N or O atoms in multi-dentate fashions to stabilize coordination highly unsaturated rare-earth metal ions. In contrast, easily accessible and mono-dentate arylamido frameworks as ancillary ligand in the coordination/organometallic chemistry of rare-earth metals are far less explored, despite that the steric and electronic environments of arylamido ligands are also ready to be tuned facilely by the variation of substituents on both the phenyl ring and nitrogen atom.[2] To our knowledge, since Schumann and co-workers firstly reported the preparation of bis(arylamido) rare-earth metal chloride complexes and tris(arylamido) rare-earth metal complexes in 1995,[2i] much attention were paid to reveal the coordination modes of arylamido ligands to central rare-earth metals, while the studies on the reactivity of arylamido-ligated rare-earth metal complexes are still relatively limited.[2b,c,f,g]

Owing to the diversity of structural feature and the comparable bond disruption enthalpy of amide groups, recently, rare-earth metal amide complexes (Ln–N σ-bonded complexes) are expected to possess unique reactivity.[3-5] We recently found that rare-earth metal bis(amide) complexes could act as facilely accessible and thermally stable catalyst precursors in stereo-specific polymerization.[6] To gain a better understanding of the performance of rare-earth metal bis(amide) complexes in the polymerization, especially to reveal the effect of ancillary ligands on the polymerization, we become interested in exploring the chemistry of mono-arylamido-ligated rare-earth metal bis(silylamide) complexes. It was found that the neutral rare-earth metal bis(silylamide) complexes could be obtained in high yields by one-pot salt metathesis from $LnCl_3$, arylamido lithium and amide lithium, and could serve as active catalyst precursors for isoprene polymerization in the presence of $[Ph_3C][B(C_6F_5)_4]$ and AlR_3. Treatment of the rare-earth metal bis(silylamide) complexes with excess $AlMe_3$ provided the heterobimetallic Ln-Al methyl complexes, which may elucidate the essential role of AlR_3 in the polymerization. Here we wish to report there results.

Results and discussion

Synthesis and characterization of mono-arylamido-ligated rare-earth metal bis(silylamide) complexes. One-pot salt metathesis reaction of $LnCl_3$ with one equivalent of arylamido lithium $[2,6\text{-}{}^iPr_2C_6H_3N(SiMe_3)]Li$, followed by addition of two equivalents of $LiN(SiHMe_2)_2$ in THF at room temperature, after workup, gave the neutral mono-arylamido-ligated rare-earth metal bis(silylamide) complexes $[2,6\text{-}{}^iPr_2C_6H_3N(SiMe_3)]Ln[N(SiHMe_2)_2]_2(THF)$ (Ln = Y (**1**), Lu (**2**), La (**3**)) in

92-97% isolated yields, as shown in Scheme 1. However, it is difficult to obtain complexes **1-3** by amine elimination between Ln[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ and 2,6-iPr$_2$C$_6$H$_3$NH(SiMe$_3$) at room temperature, even under prolonged reaction time (48 h) and at elevated temperature (100 °C).

Elemental analysis, FT-IR spectroscopy and NMR spectroscopy of **1-3**, together with single crystal X-ray crystallography of **2** showed that these complexes are neutral and mononuclear species. These complexes are soluble in THF, toluene and diethyl ether, but sparingly soluble in hexane.

Single crystals of **2** suitable for X-ray diffraction were grown from a mixture solution of toluene and hexane at –30 °C. The molecular structure with selected bond distances and bond angles is shown in Fig. 1. The short bond distance of Lu–H(3)(Si3) (2.44(4) Å) indicates there exists η^2(Si-H) interactions resulting from the agnostic Si–H–Lu interaction in the solid-state structure of **2**.[7] The center metal is five-coordinated to an arylamido ligand through the nitrogen atom in η^1-fashion, two silylamide groups one agnostic H atom, and one THF molecule to adopt a distorted-trigonal-bipyramidal geometry. The phenyl ring of the arylamido ligand is oriented almost parallel to the plane formed by N(2), N(3) and O(1), which may provide a suitable steric hindrance in control of stereo-specific insertion of isoprene in the polymerization (*vide infra*).[2b] The Lu–N (arylamido) bond distance in **2** (2.183(3) Å) is consistent with that in the mono-arylamido-ligated lutetium bis(alkyl) complex [2,6-^{i}Pr$_2$C$_6$H$_3$N(SiMe$_3$)]Lu(CH$_2$SiMe$_3$)$_2$(THF) (2.153(2) Å).[2b] The Lu–N(SiHMe$_2$)$_2$ distances in **2** are 2.196(3) and 2.186(3) Å, which are comparable with those in non-Cp rare-earth metal complexes, such as $[PhC(N\text{-}2,6\text{-}^iPr_2C_6H_3)_2]Sc[N(SiHMe_2)_2]_2$ (2.065(3) Å),[6g] $[TolC(N\text{-}2,6\text{-}^iPr_2C_6H_3)_2]Y[N(SiHMe_2)_2]_2(THF)$ (2.250(3) and 2.258(3) Å),[8] and mono(aminopyridinate)$Sc[N(SiHMe_2)_2]_2$ (average 2.049 Å),[9] if the differences in radii and coordination number are considered.[10]

Insert Scheme 1, and Fig. 1 herein

Isoprene polymerization employing the mono-arylamido-ligated rare-earth metal bis(silylamide) complexes as catalyst precursors. To evaluate the polymerization property of these rare-earth metal bis(amide) complexes, they were employed as catalyst precursors in isoprene polymerization. These neutral rare-earth metal bis(silylamide) complexes **1**-**3** alone showed no activity toward isoprene polymerization. However, upon activation by 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ in toluene, they became active for isoprene polymerization with the activity trend of **3** > **2** >> **1**, and produced poly(isoprene) with high *cis*-1,4-selectivity (> 96%) (Table 1, runs 1-3). The polymerization selectivity was different to that promoted by another amidinato-ligated non-Cp rare-earth metal amide catalyst systems $[PhC(N\text{-}2,6\text{-}R_2C_6H_3)_2]Ln[N(SiHMe_2)_2]_2/[Ph_3C][B(C_6F_5)_4]$,[6e,g] which produced poly(isoprene) with 3,4-selectivity, suggesting a strong ligand effect on the polymerization performance. However, even with the highest active catalyst system **3**/$[Ph_3C][B(C_6F_5)_4]$, the conversion reached only up to 70% in 10 h at the initial feed ratio [M]/[Ln] = 500 (Table 1, run 3). Meanwhile, the combination of **1**-**3** with $B(C_6F_5)_3$ or $[PhNMe_2H][B(C_6F_5)_4]$ could hardly initiated the detectable isoprene polymerization. This may contribute to $B(C_6F_5)_3$ was not Lewis acid strong enough to ionize the complexes, and the byproduct $PhNMe_2$ of the reaction between the complexes and $[PhNMe_2H][B(C_6F_5)_4]$ disintegrated the cationic species upon coordination to the rare-earth metal center.

Remarkably, addition of AlR_3 to **1-3**/$[Ph_3C][B(C_6F_5)_4]$ catalyst systems dramatically increased polymerization activity. The polymerization activity was significantly dependent on the type of AlR_3. For example, employing **2** as the catalyst precursor, it took nearly 1 h to get 100% conversion when AlR_3 was $AlMe_3$. In comparison, using Al^iBu_3 instead of $AlMe_3$, 100% conversion was observed in 5 min (Table 1, runs 6 and 7). Increasing of [Al]/[Ln] molar ratio from 5 to 20 had little effect on regio-selectivity, but led to the decreasing in the molecular weight of the polymers from $M_n = 4.2$ to 2.8×10^4, indicative of Al^iBu_3 also playing the role of chain-transfer agent during the polymerization (Table 1, runs 6, 9 and 10). The activity could compete for the most active *cis*-1,4 isoprene polymerization catalyst systems, such as $[PhC(N\text{-}2,6\text{-}R_2C_6H_3)_2]Ln[N(SiHMe_2)_2]_2/[Ph_3C][B(C_6F_5)_4]/AlMe_3$[6e,g], $[PhC(N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2]Y(CH_2C_6H_4NMe_2\text{-}o)_2/[Ph_3C][B(C_6F_5)_4]/AlMe_3$[11], indolyl-ligated rare-earth monoalkyl complexes/$[Ph_3C][B(C_6F_5)_4]/AlR_3$[12], $Ln[(N(SiMe_3)_2]_3$/borate/Al^iBu_3[13], $(3,6\text{-}({}^tBu)_2\text{-}1,8\text{-}(PPh_2)_2\text{-carbazole})Y(C_6H_4CH_2N(Me)_2)_2/[Ph_3C][B(C_6F_5)_4]$[14], and $(2,6\text{-}(2,6\text{-}C_6H_3R_2N{=}CH)_2C_6H_3)LnCl_2(THF)_2/[Ph_3C][B(C_6F_5)_4]/AlR_3$[15]. NMR spectroscopy showed that the ternary catalyst systems also afforded polymers with highly *cis*-1,4 regio-specificity, which increased with the increase of rare-earth metal size (Table 1, runs 4, 6 and 8). This result was consistent with those reported previously that the reduced steric encumbrance at the larger metal centers facilitated the 1,4-enchainments.[16] Notably, the *cis*-1,4 selectivity could reach up to 99% when the polymerization was carried out at 0 °C, and a reasonable selectivity was still observed at a high temperature (60 °C) (Table 1, runs 11 and 12). Meanwhile, the isolated heterobimetallic Ln/Al methyl complexes **4-6** were capable to promote *cis*-1,4 isoprene polymerization in the presence of one equivalent of $[Ph_3C][B(C_6F_5)_4]$ with reasonable catalytic activity compared to the corresponding ternary catalyst systems (Table 1, runs 16-18).[17] It was noteworthy that a quasi-living polymerization fashion was observed in the molar ratio range of [M]/[Lu] from 500 to 2000 using **2**/$[Ph_3C][B(C_6F_5)_4]$/Al^iBu_3 as the catalyst system, for the molecular weights of the resulting polymers increased almost linearly with the increase of the molar ratio of monomer-to-initiator, while the molecular weight distributions M_w/M_n kept narrow (1.18-1.26) (Table 1, runs 6, 13-15). GPC curves indicated that the polymer samples produced by either the binary catalyst systems or the ternary catalyst systems were all unimodal, indicative of a single-site polymerization behavior.

Insert Table 1 herein

Reaction of mono-arylamido-ligated rare-earth metal bis(silylamide) complexes with $AlMe_3$. Since the introduction of AlR_3 into the binary catalyst systems increased the polymerization activity, we became interested in the reaction of **1-3** with $AlMe_3$ in order to disclose the essential role of AlR_3 in the polymerization. Usually, the third component of alkylaluminum compound AlR_3 serves not solely as a scavenger or a co-catalyst, it may also dramatically affect the polymerization activity and change the active species in the polymerization.[11] Because there are three Ln-N σ-bonds in these arylamido-ligated rare-earth metal bis(silylamide) complexes, it raises the intriguing question of which Ln-N σ-bond actually participates in the reaction when they are combined with $AlMe_3$. Towards this end, treatment of **1**-**3** with excess $AlMe_3$ in toluene at room temperature, after workup, afforded the mono-arylamido-ligated Ln/Al heterometallic methyl complexes $[2,6\text{-}^i Pr_2C_6H_3N(SiMe_3)]Ln[(\mu\text{-}Me)_2AlMe_2]_2$ (Ln = Y (**4**), Lu (**5**), La (**6**)) in 59-68% isolated yields (Scheme 2). This result showed that amide-alkyl exchange occurred between two σ-bonded silylamide groups and $AlMe_3$, whilst the arylamido ligand was still coordinated to the rare-earth metal. The concomitant byproducts of arylamido ligand transfer from rare-earth metal to Al was not observed.[18] Complexes **4**-**6** showed perfect solubility in common organic solvents such as THF, toluene and hexane, and were well-characterized by elemental analysis, FT-IR spectroscopy and NMR spectroscopy. Single crystal X-ray diffraction of **4** and **5** revealed that the complexes could be viewed as a combination of one molecule of $[2,6\text{-}^i Pr_2C_6H_3N(SiMe_3)LnMe_2]$ with two molecules of $AlMe_3$, as shown in Fig. 2. Since the catalyst systems and the polymerization selectivity were quite similar to those reported previously,[6g,11,19] the active species in these ternary catalyst systems were therefore proposed to be the cationic heterobimetallic Ln/Al complexes, which tended to incorporate η^4-*cis*-isoprene during the polymerization.

Insert Scheme 2 and Fig. 2 herein

Conclusions

In summary, the neutral mono-dentate arylamido-ligated rare-earth metal bis(silylamide) complexes $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Ln}[\text{N}(\text{SiHMe}_2)_2]_2(\text{THF})$ (Ln = Y, Lu, La) could be prepared by one-pot salt metathesis reaction of LnCl_3, $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Li}$ and $\text{LiN}(\text{SiHMe}_2)_2$ in 1:1:2 molar ratio in THF at room temperature. These complexes were highly active for *cis*-1,4-selective polymerization of isoprene in the presence of Al^iBu_3 and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. The ternary catalyst system of **2**/$[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Al}^i\text{Bu}_3$ showed living polymerization performance at room temperature. Treatment of $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Ln}[\text{N}(\text{SiHMe}_2)_2]_2(\text{THF})$ with excess AlMe_3 gave the mono(arylamido) heterobimetallic Ln/Al methyl complexes $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Ln}[(\mu\text{-Me})_2\text{AlMe}_2]_2$ (Ln = Y, Lu, La), which may shed a light on the essential role of rare-earth metal bis(silylamide) complexes employed in the polymerization.

Experimental section

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 and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ were purchased from Strem. Al^iBu_3 and AlMe_3 (1.0 M in hexane solution) were purchased from Acros. Isoprene was purchased from Acros, dried by stirring with CaH_2, and distilled before polymerization. Deuterated solvents ($CDCl_3$ and C_6D_6) were obtained from CIL. $LiN(SiHMe_2)_2$[20] and $(2,6\text{-}^i Pr_2C_6H_3)NH(SiMe_3)$[2b,g] were prepared according to the literature.

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 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; quoted data are the average of at least two independent determinations. FT-IR spectra were recorded on a Bruker TENSOR 27 spectrometer. Molecular weight and molecular weight distribution of the polymers were measured by a PL GPC 50 instrument with two Mixed-B columns at 40 °C using THF as eluent against polystyrene standards: flow rate, 1 mL/min; sample concentration, 1 mg/mL.

$[2,6\text{-}^i Pr_2C_6H_3N(SiMe_3)]Y[N(SiHMe_2)_2]_2(THF)$ (1). In a glovebox, to a THF slurry of anhydrous YCl_3 (0.976, 5 mmol) was added slowly 1 equiv of $[2,6\text{-}^i Pr_2C_6H_3N(SiMe_3)]Li$ (1.277 g, 5 mmol) in THF (30 mL) at room temperature. The mixture was stirred at room temperature for 2 h to afford a clear solution, to which $LiN(SiHMe_2)_2$ (1.393 g, 10 mmol) in THF (20 mL) was introduced via a syringe at room temperature. The resulting solution was stirred at room temperature for 24 h to give a gray solution. Removal of the volatiles under vacuum afforded pale yellow solid, which was extracted by hexane (3 × 15 mL). After hexane was removed, **1** was obtained as pale yellow sticky solid (3.11 g, 92%). Recrystallization from hexane solution at –35 °C gave **1** as colorless needle crystals. ^1H NMR (500 MHz,

C_6D_6): δ 0.36 (d, 24 H, SiH*Me*$_2$), 0.45 (s, 9 H, Si*Me*$_3$), 1.08 (br s, 4 H, THF-β-H), 1.30 (d, 6 H, CH*Me*$_2$), 1.32 (d, 6H, CH*Me*$_2$), 3.33 (br s, 4 H, THF-α-H), 3.96 (m, 2 H, C*H*Me$_2$), 4.97 (m, 4 H, Si*H*Me$_2$), 6.95 (t, 1 H, *p*-C_6H_3), 7.09 (d, 2 H, *m*-C_6H_3). ^{13}C NMR (500 MHz, C_6D_6), δ 3.6 (SiH*Me*$_2$), 3.8 (Si*Me*$_3$), 25.1 (*C*HMe$_2$), 26.0, 27.2 (CH*Me*$_2$), 26.5 (THF-β-*C*), 71.9 (THF-α-*C*), 121.9, 124.3, 145.8, 146.9 (Ar-*C*). FT-IR (KBr, cm^{-1}): 3390 m, 2960 s, 2120 m, 2080 m, 1440 s, 1330 m, 1250 s, 1200 w, 906 s, 839 s, 779 w. Anal. Calcd. for $C_{27}H_{62}N_3OSi_5Y$: C, 48.10; H, 9.29; N, 6.23. Found: C, 48.51; H, 9.32; N, 6.44.

[2,6-^{i}Pr$_2$C$_6$H$_3$N(SiMe$_3$)]Lu[N(SiHMe$_2$)$_2$]$_2$(THF) (2). Following the procedure as that for **1**. Using $LuCl_3$ (1.226, 5 mmol), [2,6-^{i}Pr$_2$C$_6$H$_3$N(SiMe$_3$)]Li (1.277 g, 5 mmol), and LiN(SiHMe$_2$)$_2$ (1.393 g, 10 mmol) to afford **2** as pale yellow sticky solid (3.7 g, 97%). Recrystallization from hexane solution at –35 °C gave **2** as colorless needle crystals. ^{1}H NMR (500 MHz, C_6D_6): δ 0.37 (d, 24 H, SiH*Me*$_2$), 0.47 (s, 9 H, Si*Me*$_3$), 1.06 (br s, 4 H, THF-β-*H*), 1.30 (d, 6 H, CH*Me*$_2$), 1.35 (d, 6 H, CH*Me*$_2$), 3.36 (br s, 4 H, THF-α-*H*), 4.03 (m, 2 H, C*H*Me$_2$), 4.97 (m, 4 H, Si*H*Me$_2$), 6.97 (t, 1 H, *p*-C_6H_3), 7.11 (d, 2 H, *m*-C_6H_3). ^{13}C NMR (500 MHz, C_6D_6), δ 3.6 (SiH*Me*$_2$), 3.9 (Si*Me*$_3$), 25.1 (*C*HMe$_2$), 26.1, 27.2 (CH*Me*$_2$), 26.6 (THF-β-*C*), 72.7 (THF-α-*C*), 121.9 124.2, 145.8, 147.7 (Ar-*C*). FT-IR (KBr, cm^{-1}): 3390 m, 2960 s, 2100 s, 2170 m, 1440 s, 1330 m, 1250 s, 1180 w, 906 s, 837 s, 785 m. Anal. Calcd. for $C_{27}H_{62}LuN_3OSi_5$: C, 42.65; H, 8.24; N, 5.53. Found: C, 42.33; H, 8.65; N, 5.20.

[2,6-^{i}Pr$_2$C$_6$H$_3$N(SiMe$_3$)]La[N(SiHMe$_2$)$_2$]$_2$(THF) (3). Following the procedure as that for **1**. Using $LaCl_3$ (1.226, 5 mmol), [2,6-^{i}Pr$_2$C$_6$H$_3$N(SiMe$_3$)]Li (1.277 g, 5 mmol), and $LiN(SiHMe_2)_2$ (1.393 g, 10 mmol)to afford **3** as deep yellow sticky solid (3.45 g, 95%). Recrystallization from hexane solution at –35 °C gave **3** as colorless needle crystals. ^1H NMR (500 MHz, C_6D_6): δ 0.38 (d, 24 H, SiH*Me*$_2$), 0.48 (s, 9 H, Si*Me*$_3$), 1.10 (br s, 4 H, THF-β-*H*), 1.26 (d, 6 H, CH*Me*$_2$), 1.27 (d, 6H, CH*Me*$_2$), 3.14 (br s, 4 H, THF-α-*H*), 3.83 (m, 2 H, C*H*Me$_2$), 5.03 (m, 4 H, Si*H*Me$_2$), 6.83 (t, 1 H, *p*-C_6H_3), 7.05 (d, 2H, *m*-C_6H_3). ^{13}C NMR (500 MHz, C_6D_6), δ 3.3 (SiH*Me*$_2$), 3.9 (Si*Me*$_3$), 25.1 (*C*HMe$_2$), 25.7, 27.3 (CH*Me*$_2$), 26.5 (THF-β-*C*), 70.4 (THF-α-*C*), 122.4, 124.9, 145.5, 147.2 (Ar-*C*). FT-IR (KBr, cm^{-1}): 3380 m, 2960 s, 2109 m, 2050 s, 1440 s, 1330 w, 1250 s, 1200 w, 904 s, 837 m, 779 m. Anal. Calcd. for $C_{27}H_{62}LaN_3OSi_5$: C, 44.78; H, 8.65; N, 5.80. Found: C, 44.46; H, 8.47; N, 5.67.

$[2,6\text{-}^iPr_2C_6H_3N(SiMe_3)]Y[(\mu\text{-}Me)_2AlMe_2]_2$ (4). A toluene (10 mL) solution of **1** (0.674 g, 1 mmol) was added dropwise to a heptane solution (6 mL) of $AlMe_3$ (6 mmol, 1.0 M) at room temperature. The reaction mixture was stirred at room temperature for 2 h to give a clear colorless solution. Removal of the volatiles under vacuum produced a white solid, which was extracted by hexane (3 × 5 mL). After the co-product of $Me_2Al[(\mu\text{-}N(SiHMe_2)_2]_2AlMe_2$ was separated from hexane solution by the fractional recrystallization, the residue mother solution was dried up in vacuum. The resulting pale yellow powder was dissolved in hexane and filtered. Concentrating and cooling the filtrate gave **4** as colorless crystals (0.32 g, 63%). ^1H NMR (500 MHz, C_6D_6): δ -0.23 (d, 24 H, C*H*$_3$), 0.25 (s, 9 H, Si*Me*$_3$), 1.02 (d, 6 H, CH*Me*$_2$), 1.16 (d, 6 H, CH*Me*$_2$), 3.33 (m, 2 H, C*H*Me$_2$), 7.02 (m, 3H, C_6H_3). ^{13}C NMR (500 MHz, C_6D_6), δ 1.5 (Si*Me*$_3$), 3.8 (*C*H$_3$), 23.6 (*C*HMe$_2$), 26.6, 28.3 (CH*Me*$_2$), 126.0, 126.3, 138.8, 148.7 (Ar-*C*). FT-IR (KBr, cm^{-1}): 3380 w, 3050 m, 2960 s, 1460 s, 1420 s, 1380 m,1310 m, 1250 s, 1190 s, 1110 s, 1040 m, 910 m, 841 s, 700 s, 573 m, 513 m. Anal. Calcd. for $C_{23}H_{50}Al_2NSiY$: C, 53.99; H, 9.87; N, 2.74. Found: C, 54.00; H, 9.85; N, 2.83.

[2,6-^{i}Pr$_2$C$_6$H$_3$N(SiMe$_3$)]Lu[(μ-Me)$_2$AlMe$_2$]$_2$ (5). Following the procedure as that for **4**. Using **2** (0.760 g, 1 mmol) and $AlMe_3$ (6 mmol, 1.0 M)to afford **5** as clear colorless crystals (0.35 g, 59%). ^{1}H NMR (500 MHz, C_6D_6): δ -0.01 (s, 24 H, C*H*$_3$), 0.23 (s, 9 H, Si*Me*$_3$), 1.07 (d, 6 H, CH*Me*$_2$), 1.19 (d, 6 H, CH*Me*$_2$), 3.45 (m, 2 H, C*H*Me$_2$), 7.02 (t, 3 H, C_6H_3). ^{13}C NMR (500 MHz, C_6D_6), δ 3.1 (Si*Me*$_3$), 3.9 (*C*H$_3$), 24.1 (*C*HMe$_2$), 26.5, 28.1 (CH*Me*$_2$), 125.4, 125.5, 140.4, 147.3 (Ar-*C*). FT-IR (KBr, cm^{-1}): 3390 w, 3050 m, 2960 s, 1460 s, 1420 s, 1380 m, 1310 m, 1250 s, 1180 s, 1110 s, 1040 m, 906 m, 843 s, 696 s, 573 m, 515 m. Anal. Calcd. for $C_{23}H_{50}Al_2LuNSi$: C, 46.22; H, 8.45; N, 2.34. Found: C, 46.61; H, 8.33; N, 2.65.

[2,6-^{i}Pr$_2$C$_6$H$_3$N(SiMe$_3$)]La[(μ-Me)$_2$AlMe$_2$]$_2$ (6). Following the procedure as that for **4**. Using **3** (0.724 g, 1 mmol) and $AlMe_3$ (6 mmol, 1.0 M) to afford **6** as clear colorless crystals (0.38 g, 68%). ^{1}H NMR (500 MHz, C_6D_6): δ -0.19 (d, 24 H, SiH*Me*$_2$), 0.24 (s, 9 H, Si*Me*$_3$), 0.96 (d, 6 H, CH*Me*$_2$), 1.14 (d, 6H, CH*Me*$_2$), 3.11 (m, 2 H, C*H*Me$_2$), 6.99 (t, 1 H, *p*-C_6H_3), 7.07 (d, 2 H, *m*-C_6H_3). ^{13}C NMR (500 MHz, C_6D_6), δ 3.2 (*C*H$_3$), 3.4 (Si*Me*$_3$), 26.4 (*C*HMe$_2$), 27.7, 28.5 (CH*Me*$_2$), 122.8, 123.6, 146.4, 147.2 (Ar-*C*). FT-IR (KBr, cm^{-1}): 3390 w, 3050 m, 2960 s, 1460 s, 1420 s, 1380 m, 1310 m, 1250 s, 1180 s, 1110 s, 1040 m, 904 m, 846 s, 698 s, 573 m, 517 m. Anal. Calcd. for $C_{23}H_{50}Al_2LaNSi$: C, 49.18; H, 8.99; N, 2.49. Found: C, 49.46; H, 8.73; N, 2.65.

Typical procedure for isoprene polymerization. The procedures for isoprene 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 the rare-earth metal complex, toluene, $Al^{i}Bu_3$, $[Ph_3C][B(C_6F_5)_4]$, 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 weighted.

X-ray crystallographic study. Suitable single crystals of complexes were sealed in a thin-walled glass capillary for determining the single-crystal structure. Intensity data were collected with a Rigaku Saturn or Xcalibur, Atlas, Gemini CCD area detector in ω scan mode using Mo Kα radiation (λ = 0.71070 Å). 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 1430243-1430245 contains the supplementary crystallographic data for complexes **2**, **4** and **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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17. $Cp^RLn(AlMe_4)_2$ as the catalyst precursors for isoprene polymerization afforded *trans*-1,4 poly(isoprene)s, see: (a) M. Zimmermann, K. Tornroos and R. Anwander, *Angew. Chem., Int. Ed.*, 2008, **47**, 775. (b) M. Zimmermann, K. W. Tornroos, H. Sitzmann and R. Anwander, *Chem. Eur. J.*, 2008, **14**, 7266. (c) M. Zimmermann, J. Volbeda, K. W. Tornroos and R. Anwander, *C. R. Chim.*, 2010, **13**, 651.

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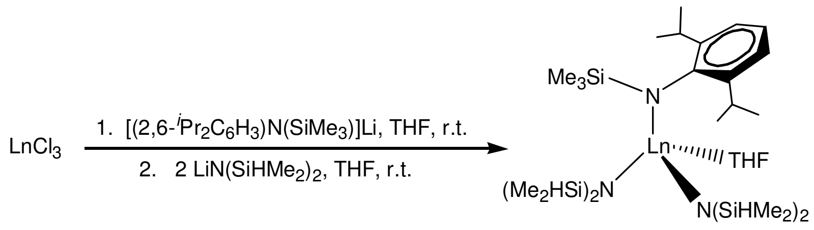
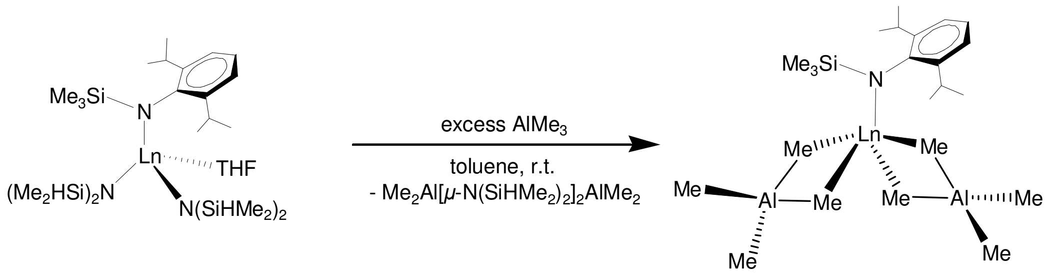


Ln = Y (**1**), Lu (**2**), La (**3**)

Scheme 1 Synthesis of mono-arylamido-ligated rare-earth metal bis(silylamide) complexes



Ln = Y (**4**), Lu (**5**), La (**6**)

Scheme 2 Synthesis of mono-arylamido-ligated heterometallic Ln/Al methyl complexes

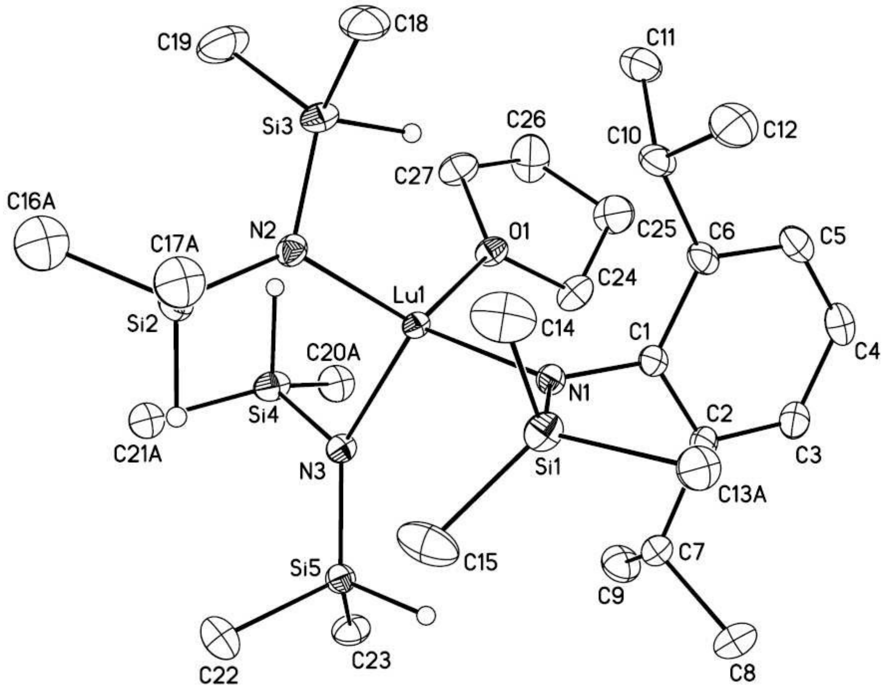


Fig. 1 Molecular structure of **2**. Hydrogen atoms (except those on SiH) are omitted for clarity. Selected bond lengths (Å) and angles (°): Lu1–N1 = 2.183(3), Lu1–N2 = 2.196(3), Lu1–N3 = 2.186(3), Lu1–H3 = 2.44(4), Lu1–O1 = 2.320(2), N1–Lu1–N2 = 107.35(10), N1–Lu1–N3 = 113.58(10), N1–Lu1–O2 = 105.19(9), N2–Lu1–N3 = 106.84(11).

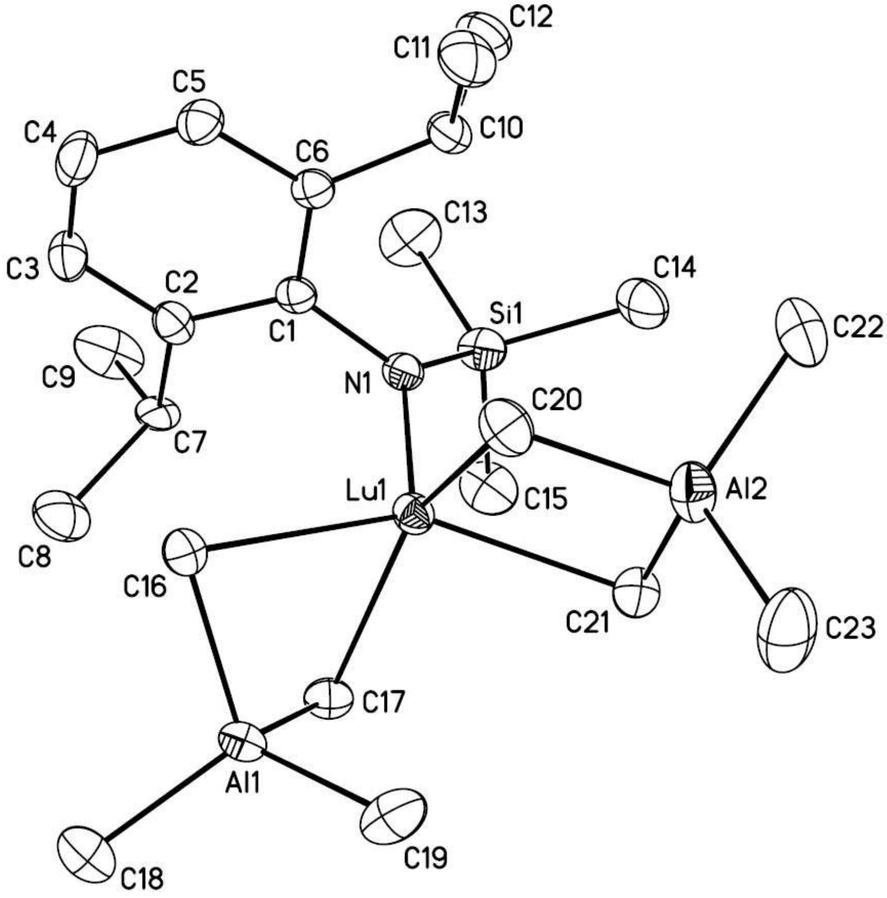


Fig. 2 Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Lu1–N1 = 2.120(3), Lu1–C16 = 2.570(5), Lu1–C17 = 2.520(4), Lu1–C20 = 2.474(5), Lu1–C21 = 2.450(6), Al1–C16 = 2.070(5), Al1–C17 = 2.073(5), Al1–C18 = 1.934(6), Al1–C19 = 1.968(5), Al2–C20 = 2.075(6), Al2–C21 = 2.077(6), Al2–C22 = 1.957(5), Al2–C23 = 1.948(6), C1–N1–Si1 = 123.9(3), C16–Lu1–C17 = 80.45(16), C20–Lu1–C21 = 85.04(19), C16–Al1–C17 = 105.0(2), C18–Al1–C19 = 118.3(3), C20–Al2–C21 = 106.6(2), C22–Al2–C23 = 116.2(3).

Table 1 Polymerization of isoprene using complexes **1-6** under various conditions[a]

run	complex	[M]/[Ln]	AlR_3	temp (ºC)	*t* (min)	yield[b] (%)	M_n[c] ×10^{-4}	M_w/M_n[c]	1,4-/3,4-[d] (%)
1	**1**	500	-	15	600	trace	-	-	-
2	**2**	500	-	15	600	36	6.9	1.65	96/4
3	**3**	500	-	15	600	70	5.7	1.61	98/2
4	**1**	500	Al^iBu_3(5)	15	20	100	6.2	1.53	97/3
5	**1**	500	$AlMe_3$(5)	15	60	93	5.8	1.66	95/5
6	**2**	500	Al^iBu_3(5)	15	5	100	4.2	1.22	96/4
7	**2**	500	$AlMe_3$(5)	15	60	100	5.4	1.60	93/7
8	**3**	500	Al^iBu_3(5)	15	10	100	6.1	1.69	99/1
9	**2**	500	Al^iBu_3(10)	15	5	100	3.9	1.38	97/3
10	**2**	500	Al^iBu_3(20)	15	5	100	2.8	1.42	98/2
11	**2**	500	Al^iBu_3(5)	0	20	100	5.1	1.31	99/1
12	**2**	500	Al^iBu_3(5)	60	5	100	4.6	1.52	95/5
13	**2**	1000	Al^iBu_3(5)	15	10	100	7.8	1.25	97/3
14	**2**	1500	Al^iBu_3(5)	15	10	100	11.9	1.18	98/2
15	**2**	2000	Al^iBu_3(5)	15	10	100	15.6	1.26	97/3
16	**4**	500	-	15	60	96	6.1	1.58	96/4
17	**5**	500	-	15	60	100	4.3	1.65	97/3
18	**6**	500	-	15	60	100	7.1	1.73	98/2

[a] Polymerization conditions: in toluene; Ln, 20 μmol, solvent/monomer = 3/1 (v/v), $[Ln]/[Ph_3C][B(C_6F_5)_4]$ = 1:1 (mol/mol). [b] Yield = weight of polymer obtained/weight of monomer used. [c] Determined by GPC in THF at 40 °C against polystyrene standard. [d] Determined by ^1H NMR in $CDCl_3$.

Table of Contents

Rare-earth metal bis(silylamide) complexes supported by mono-dentate arylamido ligand: synthesis, reactivity, and catalyst precursors in living *cis*-1,4-selective polymerization of isoprene

Liqin Shi, Qi Su, Jue chen, Xiaonian Li and Yunjie Luo*

One-pot salt metathesis reaction of $LnCl_3$, $[2,6\text{-}^iPr_2C_6H_3N(SiMe_3)]Li$ and $LiN(SiHMe_2)_2$ in 1:1:2 molar ratio gave the mono-arylamido-ligated rare-earth metal bis(silylamide) complexes $[2,6\text{-}^iPr_2C_6H_3N(SiMe_3)]Ln[N(SiHMe_2)_2]_2(THF)$ (Ln = Y, Lu, La), which showed high activity towards *cis*-1,4 selective polymerization of isoprene in the presence of $[Ph_3C][B(C_6F_5)_4]$ and Al^iBu_3.