

Aminopyridinate-Stabilized Lanthanoid Complexes: Synthesis, Structure and Polymerization of Ethylene and Isoprene

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A series of aminopyridinate-stabilized dialkyl-lanthanoid complexes has been synthesized and characterized. The complexes were prepared by alkane elimination reacting $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$ ($\text{Ln} = \text{Er}, \text{Yb}, \text{Lu}$) or $[\text{Ln}(\text{CH}_2\text{Ph})_3(\text{thf})_3]$ ($\text{Ln} = \text{Y}, \text{Er}, \text{Lu}$) with one equivalent of the bulky aminopyridine (2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)-pyridin-2-yl]amine. Single-crystal X-ray analyses were carried out for all of the benzyl derivatives. The reaction of these compounds with ammonium borate leads to the elimination of one of the two alkyl functions and affords organolanthanoid cations. The aminopyridinate-stabilized dialkyl-lan-

thanoid compounds can initiate the polymerization of isoprene after activation with perfluorinated tetraphenyl borates. The obtained polymers have a 3,4-content of 60–95 %. The metal ion size as well as the addition of alkylaluminium compounds influences the microstructure of the obtained polymer. Aminopyridinate-stabilized organolanthanoid cations of Sc, Lu, Er and Y can polymerize ethylene in the presence of alkylaluminium compounds. The Lu, Er and Y complexes act as a CCTP catalyst and the erbium compound exhibits the highest activity.

Introduction

Cationic rare earth metal alkyl compounds (mainly generated by the reaction of neutral di- or trialkyl complexes with perfluorinated borate compounds) are known to be useful initiators/catalysts for the polymerization of olefins or 1,3-dienes.^[1] One advantage of rare earth catalysts in comparison to other (for instance, group 4) metal alkyl cation catalysts is the fine tuning of the catalysts activity and/or selectivity by varying the size of the rare earth atom. For instance, Bambirra et al.^[2] as well as Okuda and co-workers^[3] imposingly demonstrated the relation between polymerization activity and the metal ion size.

Herein we report the synthesis and structure of bis(trimethylsilylmethyl) and dibenzyl rare earth complexes stabilized by bulky aminopyridinato^[4–8] (Ap) ligands. In addition, the performance of these compounds as precatalysts for the polymerization of ethylene and isoprene will be discussed. The focus will be put on the influence of the ionic radius of the rare earth atom on the activity and selectivity of the polymerization reactions as well as the ability of these compounds to mediate coordinative chain-transfer polymerisation (CCTP)^[9] of ethylene.

Isoprene polymerisation using cationic rare earth initiators has become an intensively investigated area^[10–13] after the initiating reports of Okuda and co-workers^[14] as well as Hou and co-workers.^[15]

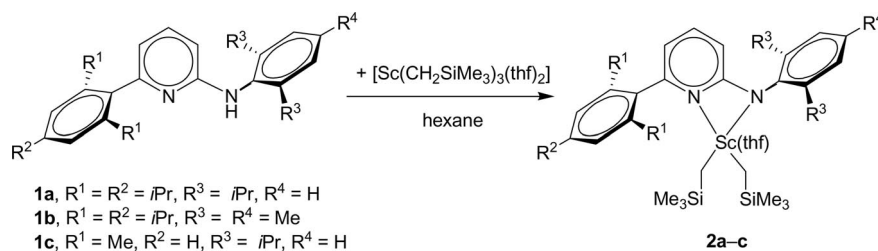
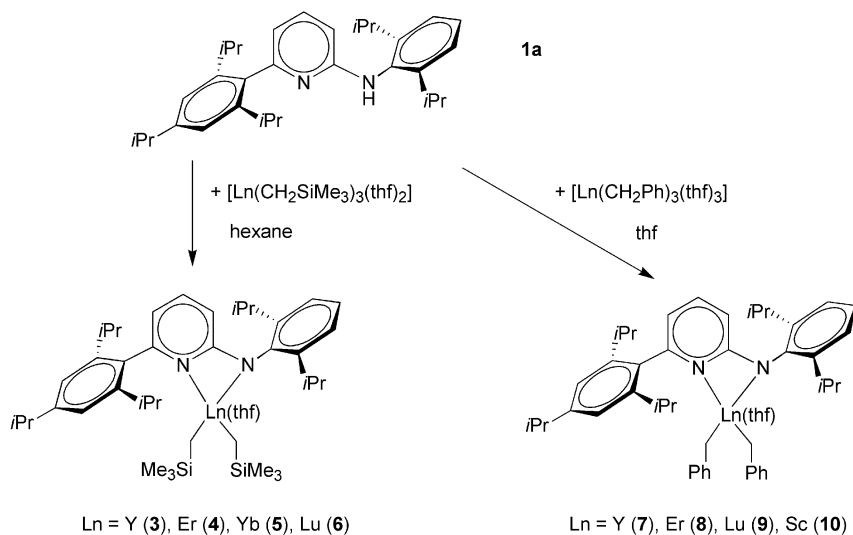
CCTP is an excellent tool to polymerize ethylene and α -olefins in a highly controlled and efficient fashion. A variety of systems are described which are capable of catalyzing this type of chain growing at main group metals or Zn.^[16]

Results and Discussion

Metal Complex Synthesis

As we reported recently, a series of aminopyridinate-stabilized bis(trimethylsilylmethyl)scandium complexes were synthesized via alkane elimination (Scheme 1).^[8] Similarly the reaction of the trialkyl precursor compounds $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(\text{thf})_2]$ ($\text{Ln} = \text{Y}, \text{Er}, \text{Yb}, \text{Lu}$) and $[\text{Ln}(\text{CH}_2\text{Ph})_3(\text{thf})_3]$ ($\text{Ln} = \text{Y}, \text{Er}, \text{Lu}$) with the aminopyridine ligand **1a** yield after alkane/toluene elimination selectively the corresponding dialkyl compounds **3–10** (Scheme 2). Efforts to obtain monoaminopyridinate complexes with larger lanthanoids ($>\text{Er}$) led to a mixture of mono- and bis(aminopyridinato) complexes. The compounds **3**, **6** and **10** were already described in earlier reports.^{[7], [8], [16]} The erbium and ytterbium analogues, compounds **4** and **5** (Scheme 2, left side) were synthesized in moderate and very good yield (64% and 93%), respectively. The aminopyridinate-stabilized dibenzyl complexes **7**, **8**, and **9** (Scheme 2, right side) were obtained in 63, 85 and 56% yield, respectively. The proton NMR spectra of **7** and **9** exhibit the characteristic splitting pattern of the aminopyridinato ligand. In contrast to the scandium analogue **10**^[8] where the methylene groups from the two benzyl ligands exhibit an AB-system only one signal is observed in

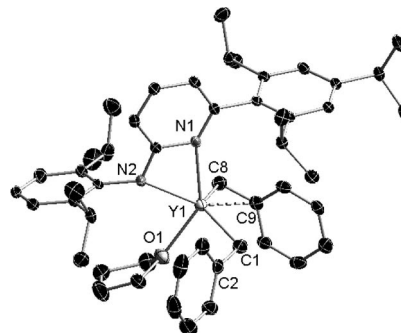
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Scheme 1. Synthesis of aminopyridinate-stabilized dialkylscandium compounds **2a–c**.Scheme 2. Synthesis of aminopyridinate-stabilized dialkyl-lanthanoid compounds **3–10**.

the ^1H NMR spectra of **7** and **9**, whereas the signal of **9** appears as a broad singlet. The ^{13}C NMR spectra show only one resonance for the methylene groups of the benzyl ligands at 54.1 (doublet, $^1J(\text{Y},\text{C}) = 28.6$ Hz) for **7** and 59.1 ppm for compound **9**, respectively.

The compounds **7–9** were also characterized by X-ray structure analysis. Suitable crystals were obtained by cooling a saturated pentane or hexane solution to 0°C . The complexes **7–9** are isostructural and crystallize in the monoclinic space group $C2/c$. The structures are depicted in Figures 1 and 2, crystallographic details are summarized in Table 4. The metal atoms are five-coordinate by one aminopyridinato ligand, one thf ligand and two benzyl ligands which show (in the solid state) different coordination modes.

Similar to the scandium derivative **10**^[8] one of the two benzyl ligands has a η^1 -coordination [Ln1–C1–C2 : 116.0(3) (**7**), 116.2(4) (**8**), 119.5(5) (**9**) and 121.88(16)° (**10**)], whereas the other ligand exhibits an η^2 -coordination which is indicated by the decreased Ln1–C8–C9 angles of 83.2(3) (**7**), 84.4(4) (**8**), 85.4(4) (**9**) and 88.50(15)° (**10**) and a shortened distance of the lanthanoid atom to the *ipso*-carbon atom of this ligand [Ln1–C9 : 2.675(4) (**7**), 2.677(6) (**8**) and 2.668(6) (**9**) Å]. Within the series **7–10** the N1–Ln1–N2 bite angle of the aminopyridinato ligand decreases with an increasing ionic radius of the metal centre^[17] from scandium to yt-

Figure 1. Molecular structure of **7** (ellipsoids set at 40% probability level). H atoms have been omitted for clarity.

trium [N1–Ln1–N2 : 57.25(12) (**7**), 57.69(15) (**8**), 58.33(15) (**9**) and 61.31(7)° (**10**)]. Another significant effect of similar nature is the decreasing Ln1–C8–C9 angle of the η^2 -coordinated benzyl ligand with increasing ionic radius (Table 1).

The dialkyl complexes **2a**, **3** and **7–10** react with one equivalent of ammonium borate in thf to afford after alkane elimination the thf stabilized organolanthanoid cations **11–14** respectively (Scheme 3). The alkyl complexes **11**, **12** and **14** have been already characterized in our previous reports.^[8,16] The organoerbium cation **13** was characterized by an X-ray structure analysis. Suitable single crystals were

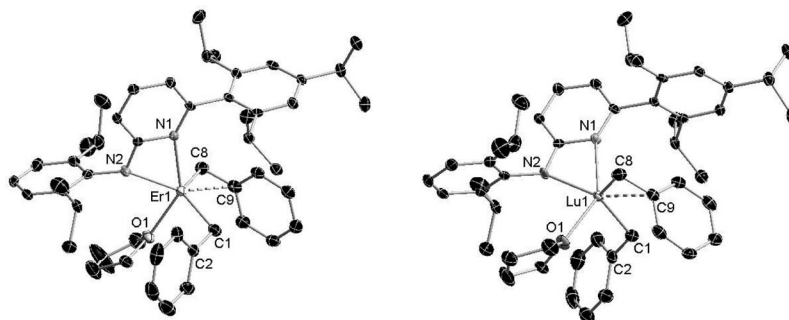


Figure 2. Molecular structure of **8** (left) and **9** (right) (ellipsoids set at 40% probability level). H atoms and solvent molecules have been omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for the complexes [Ap*Ln(CH₂Ph)₂(thf)] (Ln = Y, Er, Lu, Sc).

	Ln = Y (7)	Ln = Er (8)	Ln = Lu (9)	Ln = Sc (10) ^[a]
Bond length				
Ln1–N1	2.423(4)	2.403(4)	2.381(4)	2.286(2)
Ln1–N2	2.303(3)	2.287(4)	2.244(4)	2.129(2)
Ln1–O1	2.328(3)	2.310(4)	2.294(4)	2.1728(17)
Ln1–C1	2.414(5)	2.411(7)	2.351(7)	2.245(3)
Ln1–C8	2.436(5)	2.414(7)	2.365(7)	2.256(3)
Ln1–C9	2.675(4)	2.677(6)	2.668(6)	2.657(2)
Bond angle				
Ln1–C1–C2	116.0(3)	116.2(4)	119.5(5)	121.88(16)
Ln1–C8–C9	83.2(3)	84.4(4)	85.4(4)	88.50(15)
N1–Ln1–N2	57.25(12)	57.69(15)	58.33(15)	61.31(7)

[a] From ref.^[8]

obtained by slow diffusion of pentane into a thf solution of **13**. The compound crystallizes in the triclinic space group $P\bar{1}$, crystallographic details are summarized in Table 4 and the molecular structure is presented in Figure 3. The cation of **13** shows a distorted octahedral coordination of the erbium atom indicated by O–Er–C_{benzyl} angles of 90.1(2) and 94.8(2)°. The metal atom is coordinated by three thf, one benzyl [η^1 -coordination, Er1–C1–C2 117.4(6)°] and one aminopyridinato ligand. The thf ligands show a meridonal arrangement and the methylene group of the benzyl ligand is in *trans*-position to the pyridine nitrogen atom of the aminopyridinato ligand.

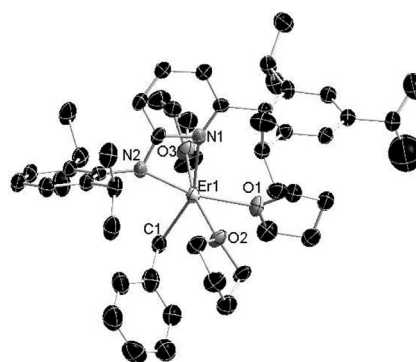
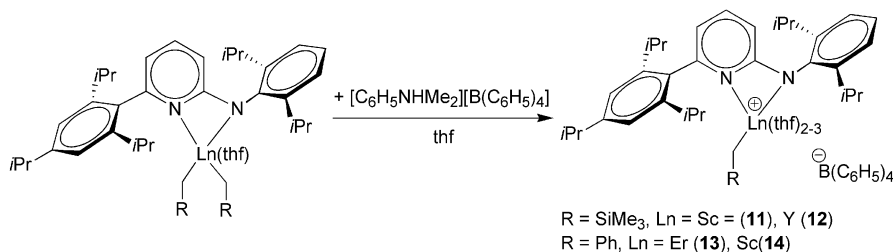


Figure 3. ORTEP diagram of the molecular structure of **13** in the solid state (ellipsoids set to 40% probability level). H atoms, solvent molecule and anion have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Er1–C1 2.418(8), Er1–N1 2.462(6), Er1–N2 2.325(6), Er1–O1 2.348(5), Er1–O2 2.317(5), Er1–O3 2.302(5), Er1–C1–C2 117.4(6), O1–Er1–C1 96.9(2), O2–Er1–C1 94.8(2), O3–Er1–C1 90.1(2).

Polymerization of Ethylene

We have recently demonstrated, that aminopyridinate-stabilized organoyttrium cations show attractive activities in the polymerization of ethylene in the presence of small amounts of alkylaluminium compounds.^[16] We could also show the influence of the steric bulk of the aminopyridinato ligand on the polymerization activity for this yttrium-based system. Therefore, we wanted to investigate the polymerization activities for other aminopyridinate-stabilized lan-



Scheme 3. Synthesis of organolanthanoid cations **11–14**.

Table 2. Polymerization of ethylene catalyzed by **2–4** under various conditions.^[a]

Run	Cat.	Alkyl-Al (equiv.)	m_{pol} [g]	M_n [g mol ⁻¹]	M_w/M_n	Activity [kg _{PE} mol _{cat} ⁻¹ h ⁻¹ bar ⁻¹]
1 ^[b]	3	TIBAO (20)	13.4	20800 ^[c]	3.2	1072
2 ^[b]	3	TIBAO (50)	4.7	3610	1.09	376
3	4	TIBAO (20)	20.2	29600	2.0	1616
4	4	TIBAO (50)	13.6	14500	1.6	1088
5	5	TIBAO (20)	0.03	n.d.	n.d.	2
6	5	TIBAO (50)	0.03	n.d.	n.d.	2
7	6	TIBAO (20)	1.6	6000	1.5	128
8	6	TIBAO (50)	0.5	n.d.	n.d.	40
9	2a	TIBAO (20)	6.7	607100 ^[c] (13100) ^[d]	3.33 (1.62)	536
10	2a	TIBAO (50)	6	610900 ^[c] (13000) ^[d]	4.71 (1.77)	480
11	2a	TIBA (25)	3.9	5150	2.71	312
12	2b	TIBAO (50)	4.8	373500 ^[c] (4280) ^[e]	16.1 (1.56)	384
13	2c	TIBAO (50)	3.9	39600	2.56	312

[a] Conditions: for dialkyl (**2–6**): 10 μmol , ammonium borate $[\text{R}_2\text{N}(\text{CH}_3)\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ($\text{R} = \text{C}_{16}\text{H}_{33}\text{--C}_{18}\text{H}_{37}$), $\text{Y/B} = 1:1.1$, 260 mL of toluene, time 15 min, temperature: 80 $^{\circ}\text{C}$, pressure: 5 bar. [b] From ref.^[8] [c] Bimodal distribution. [d] M_w of the main fraction (98%). [e] M_w of the main fraction (83%).

thanoid complexes. The compounds **2a,b,c** and **4–6** were investigated as precatalysts for the controlled ethylene polymerization (CCTP). All of these dialkyl compounds except for the yttrium derivative **5** showed low to very good activities.^[18] The erbium (**4**) and the lutetium (**6**) compounds revealed a similar dependency on the TIBAO concentration like it was already observed for the yttrium system. On the basis of this observation we suggest these compounds to be coordinative chain transfer polymerization catalysts. Whereas the lutetium compound **6** showed only low activities (Table 2, run 7, 8), the dialkylerbium compound **4** revealed the highest activities up to 1616 kg_{PE} mol_{cat}⁻¹ h⁻¹ bar⁻¹. This polymerization activity is comparable with that of other efficient CCTP catalysts, for example a $[\text{Cp}^*\text{SmCl}_2\text{Li}(\text{OEt})_2]/\text{BuMgEt}$ catalyst from Mortreux et al. (activities from 400–3070 kg_{PE} mol_{cat}⁻¹ h⁻¹ bar⁻¹)^[16c] and a bis(iminopyridine)-iron(II)/ZnEt₂/MAO catalyst system described by Britovsek et al.^[16i] with activities from 1404–1944 kg_{PE} mol_{cat}⁻¹ h⁻¹ bar⁻¹.

Because of the related ionic radii of erbium and yttrium (0.89 vs. 0.90 Å, for coordination number 6),^[17] both show high ethylene polymerization activities (Table 2, run 1–4). The activity of the erbium compound is slightly higher due to a smaller ionic radius which leads to a hampered coordination of the chain growing state.^[9a] The average number molecular weight (M_n) of the polymer obtained with the erbium compound **4** is higher than the polymer obtained with the yttrium derivative **3** (29600 and 14500 g mol⁻¹ for **4** vs. 20800 and 3610 g mol⁻¹ for **3**), whereas the molecular weight distribution remains narrow (2.0 and 1.6, Table 2, run 3, 4). When the ionic radius is decreased to 0.86 Å (coordination number 6), in the case of lutetium, the polymerization activity significantly decreased and the obtained polymer show a molecular weight of 6000 g mol⁻¹ and a relatively narrow molecular weight distribution of 1.5 (Table 2, run 7). When the scandium compound **2a** was used as a precatalyst, which comply with an ionic radius of 0.74 Å, a good activity for the polymerization of ethylene is observed. The

obtained polymer revealed a bimodal distribution, but the main fraction has a content of 98% ($M_n = 13100$, $M_w/M_n = 1.62$). In contrast to the ethylene polymerization catalysts **3**, **4** and **6**, the scandium compound **2a** did not show a significant dependency of the TIBAO concentration on the activity and the molecular weight (Table 2, run 9, 10). We suppose that the ion radius of the scandium metal is too small for the coordination of alkylaluminium compounds, which is necessary for the polyethylene chain transfer. Reduction of the steric demand of the aminopyridinato ligand leads to a decreased activity (Table 2, run 10, 12, 13), the same effect was observed for the yttrium compound, and can be explained by ligand redistribution (Figure 4).^[16i]

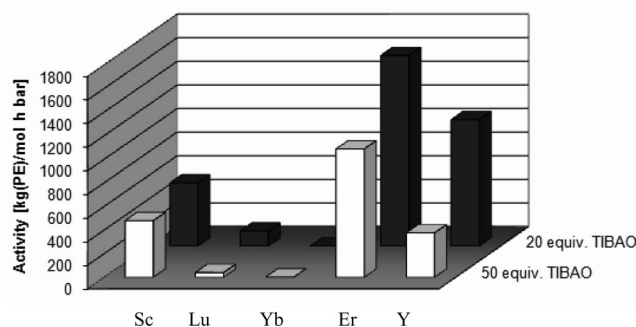


Figure 4. Influence of the metal ion size and the Al concentration on the ethylene polymerization activity.

Polymerization of Isoprene

As we have described very recently, the aminopyridinate-stabilized dialkyl compounds of scandium (**2a–c** and **10**) are active and selective catalysts for the controlled 3,4-selective polymerization of isoprene.^[8] In order to investigate the influence of the metal centre on the selectivity of the isoprene polymerization we also tested the complexes **3–9** as precatalysts for the isoprene polymerization. The microstructure of the obtained polyisoprene was determined by ¹H and ¹³C

NMR spectroscopy. The results of the polymerization experiments are summarized in Table 3. The bis(trimethylsilylmethyl)lanthanoid compounds **3**, **4** and **6** polymerize isoprene after activation with perfluorinated ammonium borate in chlorobenzene or toluene (Table 3, run 1, 2 and 4). Only the ytterbium derivative in this series is unable to initiate the polymerization of isoprene after activation (Table 3, run 3). Presumably a reduction of the ytterbium metal is an issue as indicated by a colour change of the dialkyl during the formation of the cation. The polymerization activities are comparable with that of **2a**.^[8] The thf-stabilized organoerbium cation **13** does not polymerize isoprene, even not in the presence of 10 equiv. of $\text{Al}(\text{iBu})_3$. The microstructure of the polymer obtained with **2–4** and **6** as precatalysts depends significantly on the metal size: with an increasing ionic radii of the metal centre the *cis*-1,4-polyisoprene content is increasing and the 3,4-polyisoprene content is decreasing respectively [3,4-content: 60% (Y) < 80% (Er) < 86% (Lu) < 93% (Sc)]. The same influence of the ionic radius of the central metal atom on the 3,4-selectivity was also observed by Cui and co-workers [the 3,4-content decreases from 88.5% (Sc) to 43.8% (Y)].^[10] GPC analyses of these polymers show bimodal molecular weight distributions. When the new dibenzyl complexes **7–9** are used as precatalysts for the polymerization of isoprene the same relation between the ionic radii and the microstructure, as it was described above for the bis(trimethylsilylmethyl)lanthanoid compounds, is observed (Figure 5).

Table 3. Effect of Ln size and alkyl ligand on the polymerization^[a] of isoprene.

Run	Cat.	Cocatalyst	Yield [%]	$M_n \times 10^{-3}$ [g mol ⁻¹] ^[b]	M_w/M_n ^[b]	Microstructure ^[c] <i>cis</i> -1,4; <i>trans</i> -1,4/3,4
1	3	A	100	86	3.82 ^[d]	37:3:60
2	4	A	100	34	3.52 ^[d]	13:7:80
3	5	A	—	—	—	—
4	6	A	100	104	2.98 ^[d]	4:10:86
5 ^[e]	2a	A	94	135	1.26	7:0:93
6	7	B	97	157	2.45	32:0:68
7	7	B/ $\text{Al}(\text{iBu})_3$	99	86	2.66	42:0:58
8	8	B	100	222	1.80	13:3:84
9	8	B/ $\text{Al}(\text{iBu})_3$	92	57	2.57	40:0:60
10	8	B/ AlMe_3	92	112	2.90	92:0:8
11	9	B	96	168	1.65	7:0:93
12	9	B/ $\text{Al}(\text{iBu})_3$	100	24	2.43	23:5:72
13 ^[e]	10	B	97	130	1.68	5:0:95

[a] Conditions: 10 mL of $\text{C}_6\text{H}_5\text{Cl}$, catalyst: 10 μmol , cocatalyst: A = $[\text{C}_6\text{H}_5\text{NH}(\text{CH}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$, B = $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, [cat]/[cocat] 1:1, [Al]/[cat] = 10, isoprene: 10 mmol, reaction time: 20 h, $T = 20^\circ\text{C}$. [b] Determined by GPC against polystyrene standards. [c] Determined by ^1H and ^{13}C NMR spectroscopy. [d] Bimodal distribution. [e] From ref.^[8]

The molecular weight distribution of polyisoprene produced with the dibenzyl complexes **7–10** is narrow and monodisperse, compared with the molecular weight distribution of the polyisoprene produced with the bis(trimethylsilylmethyl) complexes **3–6**, but become broader with an increasing ionic radius of the lanthanoid metal [1.68 (Sc) to 2.45 Å (Y)]. A marked decrease of the 3,4-polyisoprene content and broadening of the molecular weight distribu-

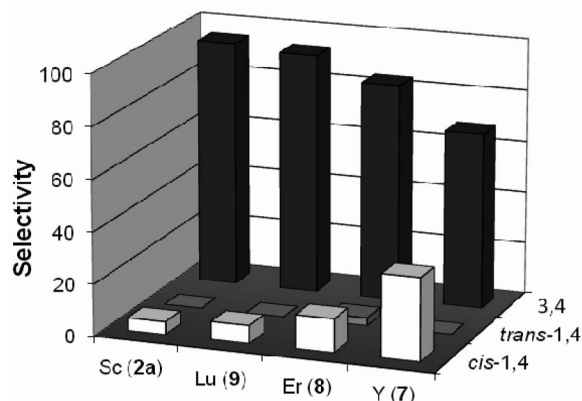


Figure 5. Influence of the metal centre on the microstructure of the obtained polyisoprene (Table 3, run 13, 11, 8, 6).

tion is observed when triisobutylaluminium (10 equiv.) was mixed with the polymerization catalyst (Table 3, see runs 7, 9 and 12). For complex **8** the polymerization was also carried out in the presence of trimethylaluminium to obtain a high *cis*-1,4-polyisoprene (92%). This effect of the alkylaluminium compounds on the microstructure of the polyisoprene was also observed for the scandium derivative **10** and an amidinato-yttrium isoprene polymerization catalyst described by Hou and co-workers.^[13]

Conclusions

Mono(aminopyridinate)lanthanoid bis(trimethylsilylmethyl) and dibenzyl complexes have been synthesized and characterized. These dialkyl-lanthanoid compounds with exception of the ytterbium compound are active catalysts for the polymerization of isoprene after activation with borates. The obtained polyisoprenes have an enriched 3,4-content. The ionic radius of the lanthanoid metal is in relation to the *cis*-1,4- to 3,4-content ratio. Smaller metals, like scandium or lutetium predominantly afford polyisoprene with high 3,4-content (>90%). The 3,4-content decreases to 68% when yttrium is used as a precatalyst. Addition of trimethylaluminium to the erbium catalyst system leads to a drastical change of the microstructure. The aminopyridinate-stabilized lanthanoid bis(trimethylsilylmethyl) compounds show very high ethylene polymerization activities in the presence of Al compounds (trialkyl compounds and aluminoxanes) and perfluorinated tetraphenyl borate. The activity is strongly influenced by the ionic radius of the lanthanoid metal. The highest activity was observed for the erbium compound. The dialkyl-ytterbium is inactive under the same conditions.

Experimental Section

General Procedures Synthesis and Structure: All reactions and manipulations involving air-sensitive compounds were performed under dry argon by using standard Schlenk and glovebox techniques. Non-halogenated solvents were dried with sodium/benzophenone

Table 4. Details of the X-ray crystal structure analyses.

Compound	7	8	9	13
Formula	C ₅₀ H ₆₅ N ₂ OY	C ₅₀ H ₆₅ ErN ₂ O·C ₅ H ₁₂	C ₅₀ H ₆₅ LuN ₂ O·C ₆ H ₁₄	C ₇₃ H ₉₀ BErN ₂ O ₃ ·OC ₄ H ₈
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	C2/c	C2/c	C2/c	P $\bar{1}$
<i>a</i> [Å]	36.7280(10)	36.7240(15)	36.8040(10)	13.6250(12)
<i>b</i> [Å]	13.0360(6)	13.0460(9)	13.0430(6)	15.2430(13)
<i>c</i> [Å]	24.1120(9)	24.1000(13)	24.0810(9)	19.1560(17)
α [°]	90	90	90	101.422(7)
β [°]	118.307(4)	118.352(5)	118.511(3)	99.138(6)
γ [°]	90	90	90	112.884(7)
<i>Z</i>	8	8	8	2
μ [mm ⁻¹]	1.180	1.689	1.982	1.258
Cell volume [Å ³]	10164.0(7)	10161.3(10)	10157.8(7)	3468.0(5)
Crystal size [mm ³]	0.36 × 0.13 × 0.09	0.25 × 0.15 × 0.08	0.32 × 0.16 × 0.11	0.58 × 0.32 × 0.14
<i>T</i> [K]	133(2)	133(2)	133(2)	133(2)
θ range [°]	1.26–26.08	1.68–26.04	1.68–25.74	1.51–25.72
Refl. unique	8666	9423	9588	13035
Refl. obsd. [<i>I</i> > 2σ(<i>I</i>)]	6447	6556	5852	7669
Parameters	487	572	548	785
<i>wR</i> ₂ (all data)	0.150	0.105	0.087	0.154
<i>R</i> value [<i>I</i> > 2σ(<i>I</i>)]	0.075	0.053	0.041	0.058

ketyl and halogenated solvents with CaH₂. Deuterated solvents were obtained from Cambridge Isotope Laboratories, degassed, dried with molecular sieves and distilled prior to use. Starting materials **1a–c**,^[7a,16f] tetraisobutylaluminumoxane ([iBu₂Al]₂O, TIBAO),^[19] [Ln(CH₂SiMe₃)₃(thf)₂],^[20] [Ln(CH₂Ph)₃(thf)₃],^[21] [LScR₂(thf)] (L = 1, R = CH₂SiMe₃, CH₂Ph),^[8] [Ap*Y(CH₂SiMe₃)₂(thf)],^[16f] [Ap*Lu(CH₂SiMe₃)₂(thf)],^[7f] [C₆H₅NH(CH₃)₂][B(C₆H₅)₄]^[22] were synthesized according to literature methods. All other chemicals were purchased from commercial sources in purities >97% and used without further purification, if not otherwise stated. NMR spectra were obtained with either a Varian INOVA 300 or a Varian INOVA 400 spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analyses were carried out with a Vario elemental EL III apparatus. The molecular weights (*M_w*/*M_n*) of the isoprene polymers were determined by gel permeation chromatography (GPC) on an Agilent 1200 series (column: PLgel Mixed-C) at 30 °C using thf as eluent and a flow rate of 1 mL/min against polystyrene standards. The molecular weights (*M_w*/*M_n*) of the ethylene polymers were determined by gel permeation chromatography on a Polymer Laboratories Ltd. (PL-GPC210 or PL-GPC220) chromatograph at 150 °C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.1% weight/volume) in the mobile phase solvent in an external oven and were run without filtration. The molecular weight was referenced to polyethylene (*M_w* = 50000 g mol⁻¹) and polystyrene (*M_w* = 100000–500000 g mol⁻¹) standards. The reported values are the average of at least two independent determinations. X-ray crystal structure analyses were performed with a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97,^[23] SHELXL-97^[24] and WinGX.^[25] Crystallographic details are summarized in Table 4.

CCDC-763799 (for **7**), -763800 (for **8**), -763801 (for **9**), -763802 (for **13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of the Complexes

Synthesis of 4: Hexane (20 mL) was added to mixture of [Er(CH₂SiMe₃)₃(thf)₂] (287 mg, 0.50 mmol) and **1a** (228 mg, 0.50 mmol).

After stirring the mixture for two hours it was filtered. After the evaporation of all volatile components **4** was yielded as an orange powder (280 mg, 64%). C₄₄H₇₃ErN₂OSi₂ (869.5): calcd. C 60.78, H 8.46, N 3.22; found C 61.17, H 8.42, N 3.61.

Synthesis of 5: The compounds [Yb(CH₂SiMe₃)₃(thf)₂] (289 mg, 0.50 mmol) and **1a** (228 mg, 0.50 mmol) were dissolved in hexane (20 mL). The mixture was stirred for two hours, subsequent filtration and removal of all volatile components yielded **5** as a red powder (405 mg, 93%). C₄₄H₇₃N₂OSi₂Yb (875.3): calcd. C 60.38, H 8.41, N 3.20; found C 60.07, H 8.14, N 3.22.

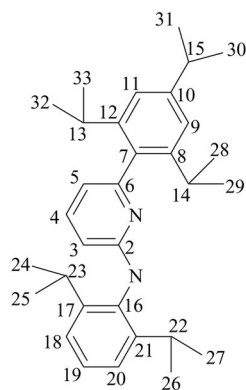
Synthesis of 7: The compounds [Y(CH₂Ph)₃(thf)₃] (463 mg, 0.80 mmol) and **1a** (365 mg, 0.80 mmol) were dissolved in thf (20 mL) and the mixture was stirred for two hours. After removal of all volatile components the residue was extracted with hexane (40 mL). The solvent was removed under reduced pressure to yield **7** as a yellow powder (400 mg, 63%). C₅₀H₆₅N₂OY (799.0): calcd. C 75.16, H 8.20, N 3.51; found C 75.00, H 8.63, N 3.42. ¹H NMR (400 MHz, C₆D₆, 298 K): δ = 1.03 (br, 4 H, β-CH₂, THF), 1.15 (d, ³J(H,H) = 6.7 Hz, 6 H, CH(CH₃)₂), 1.18 [d, ³J(H,H) = 6.9 Hz, 6 H, CH(CH₃)₂], 1.22 [d, ³J(H,H) = 6.8 Hz, 6 H, CH(CH₃)₂], 1.29 [d, ³J(H,H) = 6.9 Hz, 6 H, CH(CH₃)₂], 1.49 [d, ³J(H,H) = 6.8 Hz, 6 H, CH(CH₃)₂], 1.76 (s, 4 H, CH₂Ph), 2.86 [sept, ³J(H,H) = 6.9 Hz, 1 H, 15-H], 3.13 [sept, ³J(H,H) = 6.7 Hz, 2 H, 13,14/22,23-H], 3.25 (br, 4 H, α-CH₂, THF), 3.53 [sept, ³J(H,H) = 6.8 Hz, 2 H, 13,14/22,23-H], 5.76 [d, ³J(H,H) = 8.4 Hz, 1 H, 3-H], 6.16 [d, ³J(H,H) = 7.0 Hz, 1 H, 5-H], 6.40 [d, ³J(H,H) = 7.5 Hz, 4 H, o-H], 6.65 [t, ³J(H,H) = 7.3 Hz, 2 H, p-H], 6.84 [dd, ³J(H,H) = 8.4, ³J(H,H) = 7.0 Hz, 1 H, 4-H], 7.02 [t, ³J(H,H) = 7.6 Hz, m-H], 7.11–7.23 (m, 3 H, 18,19,20-H), 7.27 (s, 2 H, 9,11-H) ppm. ¹³C NMR (100 MHz, C₆D₆, 298 K): δ = 22.7, 22.9, 24.1, 24.3, 24.7, 28.6, 30.9, 31.8, 34.9, 54.1 [d, ¹J(Y,C) = 28.6 Hz], 70.0, 106.7, 117.5, 121.1, 121.9, 124.0, 124.9, 129.2, 131.0, 135.8, 139.2, 144.1, 144.2, 147.0, 149.9, 151.1, 155.7, 170.2 ppm.

Synthesis of 8: A mixture of [Er(CH₂Ph)₃(thf)₃] (394 mg, 0.60 mmol) and **1a** (274 mg, 0.60 mmol) were dissolved in thf (20 mL). The resulting red solution was stirred for two hours. All volatile components were removed under reduced pressure and the residue was extracted with hexane (20 mL). Removal of the solvent yield **8** as an orange crystalline compound (447 mg, 85%).

$C_{50}H_{65}ErN_2O$ (877.3): calcd. C 68.45, H 7.47, N 3.19; found C 68.14, H 7.53, N 3.42.

Synthesis of 9: $[Lu(CH_2Ph)_3(thf)_3]$ (532 mg, 0.80 mmol) and **1a** (365 mg, 0.80 mmol) were dissolved in thf (20 mL) and stirred overnight. All volatile components were removed under reduced pressure and the residue was extracted with hexane (30 mL). Removal of the solvent affords **9** as a yellow spectroscopically pure compound (400 mg, 56%). $C_{50}H_{65}LuN_2O$ (884.0): calcd. C 67.85, H 7.40, N 3.17; found C 67.63, H 7.74, N 3.33. 1H NMR (400 MHz, C_6D_6 , 298 K): δ = 0.87 (br., 4 H, β - CH_2 , THF), 1.15 [d, $^3J(H,H)$ = 6.8 Hz, 12 H, $CH(CH_3)_2$], 1.21 [d, $^3J(H,H)$ = 6.8 Hz, 6 H, $CH(CH_3)_2$], 1.30 [d, $^3J(H,H)$ = 6.9 Hz, 6 H, $CH(CH_3)_2$], 1.52 [d, $^3J(H,H)$ = 6.8 Hz, 6 H, $CH(CH_3)_2$], 1.64 (br. s, 4 H, CH_2Ph), 2.87 [sept, $^3J(H,H)$ = 6.9 Hz, 1 H, 15-H], 3.17 [sept, $^3J(H,H)$ = 6.8 Hz, 2 H, 13,14/22,23-H], 3.19 (br., 4 H, α - CH_2 , THF), 3.48 [sept, $^3J(H,H)$ = 6.8 Hz, 2 H, 13,14/22,23-H], 5.74 [d, $^3J(H,H)$ = 8.7 Hz, 1 H, 3-H], 6.22 [d, $^3J(H,H)$ = 7.1 Hz, 1 H, 5-H], 6.47 [d, $^3J(H,H)$ = 7.8 Hz, 4 H, *o*-H], 6.69 [t, $^3J(H,H)$ = 7.3 Hz, 2 H, *p*-H], 6.85 [t, $^3J(H,H)$ = 7.8 Hz, 1 H, 4-H], 7.02 [t, $^3J(H,H)$ = 7.6 Hz, *m*-H], 7.10–7.19 (m, 3 H, 18,19,20-H), 7.29 (s, 2 H, 9,11-H) ppm. ^{13}C NMR (100 MHz, C_6D_6 , 298 K): δ = 22.8, 24.2, 24.4, 24.9, 25.0, 27.0, 28.7, 31.1, 35.0, 59.1, 70.5, 106.8, 111.9, 118.2, 121.2, 123.4, 124.1, 125.3, 130.0, 135.8, 139.7, 144.0, 144.5, 147.1, 150.0, 151.3, 155.9, 169.0 ppm.

Synthesis of 13: To a mixture of **8** (132 mg, 0.15 mmol) and $[C_6H_5NH(CH_3)_2][B(C_6H_5)_4]$ (64 mg, 0.15 mmol) were added thf (2.0 mL) and toluene (1.0 mL). The reaction mixture was stirred for 5 min to obtain a clear solution. Slowly diffusion of pentane into this solution over a period of 4 d affords **13**·(OC_4H_8) as yellow crystalline plates which were separated by decanting off the solution and washed twice with pentane (2×10 mL); yield 84 mg (45%). $[C_{51}H_{74}ErN_2O_3][C_{24}H_{20}B](OC_4H_8)$ (1321.7): calcd. C 71.79, H 7.78, N 2.12; found C 71.21, H 7.54, N 2.34.



Polymerization of Ethylene: A detailed polymerization procedure (Table 2, run 1) is described as a typical example. The catalytic ethylene polymerization reactions were performed in a stainless steel 1-L autoclave, equipped with a mechanical stirrer. In a typical experiment, the autoclave was evacuated and heated for 2 h at 100 °C prior to use. The reactor was then brought to 80 °C, and charged with toluene (250 mL) together with trialkylammonium tetrakis(pentafluorophenyl)borate (11 mmol, 0.12 g) and the required amount of aluminium scavenger. After pressurizing with ethylene to reach the desired pressure, the autoclave was equilibrated for 5 min. Subsequently, the dialkyl(aminopyridinato)lanthanoid complex (1 mL, 0.01 m stock solution in toluene) was injected together with toluene (10 mL) to start the reaction. During the reaction the ethylene pressure was kept constant. After 15 min

the reactor was vented and the residual alkylaluminium compounds were destroyed by addition of 2-propanol (100 mL). The precipitated polymer was decanted and washed with acidified 2-propanol and again with 2-propanol, then dried at 80 °C to a constant weight to afford 6.5 g of polyethylene.

Polymerization of Isoprene: A detailed polymerization procedure (Table 3, run 8) is described as a typical example: in a glove box the complex **3** (8 mg, 10 μ mol) was dissolved in C_6H_5Cl (8 mL) and isoprene (680 mg, 1 mL, 10 mmol) was added. The mixture was placed in a water bath (20 °C). Then $AlMe_3$ (100 μ mol, 50 μ L, 2.0 M in hexane) and a solution of $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ (8 mg, 10 μ mol) in C_6H_5Cl (2 mL) were added. After stirring for 20 h at room temperature the mixture was poured into a large quantity of acidified 2-propanol containing 0.1 % (w/w) 2,6-di-*tert*-butyl-4-methylphenol as a stabilizing agent. The precipitated polymer was decanted, washed with 2-propanol and dried in vacuo at 60 °C to a constant weight to afford 626 mg of polyisoprene (92%). The microstructure of the polymer was examined by ^{13}C NMR spectroscopy in $CDCl_3$.

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