

Lanthanide borohydride complexes with an aryloxy ligand: Synthesis, structural characterization and polymerization activity

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Abstract

Reactions of LnCl_3 , NaBH_4 and ArONa ($\text{Ar} = \text{C}_6\text{H}_2\text{-}t\text{-Bu}_{3-2,4,6}$) in a molar ratio of 1:3:1 in THF afforded the aryloxy lanthanide borohydrides of $(\text{ArO})\text{Ln}(\text{BH}_4)_2(\text{THF})_2$ ($\text{Ln} = \text{Yb}$ (**1**), Er (**2**)). They were characterized by elemental analysis, infrared spectrum and X-ray crystallography. The two complexes are neutral and isostructural. The lanthanide atom is nine-coordinated by an aryloxy ligand, two borohydride ligands and two THF ligands in a trigonal bipyramidal geometry. Both of the BH_4 ligands in each monomeric complex are η^3 -coordinated. These complexes displayed moderate high catalytic activities for the polymerization of methyl methacrylate. The polymerization temperature had great influence on the catalysis. At about 0°C , the catalysts showed the polymerization activity best. © 2006 Elsevier B.V. All rights reserved.

Keywords: Aryloxy; Lanthanide; Borohydride; Polymerization

1. Introduction

The chemistry of lanthanide borohydrides is an important part of organolanthanide chemistry. Although the synthesis of homoleptic $\text{Ln}(\text{BH}_4)_3$ has been known for a long time [1], the chemistry of lanthanide borohydrides has remained relatively undeveloped, especially when compared with that of alkyl [2] and amido [3] lanthanide complexes. Some lanthanide borohydride complexes have been synthesized and structurally characterized including $\text{Y}(\text{BH}_4)_3(\text{THF})_3$ [4], $[(t\text{-Bu}_2\text{C}_5\text{H}_3)_2\text{Ln}(\text{BH}_4)]_2$ ($\text{Ln} = \text{Ce}$ [5], Sm [6]), $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Ln}(\text{BH}_4)$ ($\text{Ln} = \text{Y}$ [7], Yb [7], Pr [8], Nd [8]), $(\text{CH}_3\text{OCH}_2\text{CH}_2\text{C}_9\text{H}_6)_2\text{Ln}(\text{BH}_4)$ ($\text{Ln} = \text{Y}$, La) [9], $[(\text{C}_{13}\text{H}_8)\text{CPh}_2(\text{C}_5\text{H}_4)]\text{Ln}(\text{BH}_4)_2[\text{Li}(\text{THF})_4]$ ($\text{Ln} = \text{La}$, Nd) [10], $[(\text{COT})\text{Nd}(\text{BH}_4)(\text{THF})]_2$ ($\text{COT} = \text{C}_8\text{H}_8$) [11] and so on. Most of them were supported by traditional cyclopentadienyl ligands. Attempt to extend the lanthanide borohydride chemistry beyond the traditional

realm of metallocene complexes promoted us to try the synthesis of lanthanide borohydrides with aryloxy ligand, for aryloxy ligands are strongly bonded with lanthanide elements and can be steric fine tuned by the judicious choice of the substituents. Aryloxy lanthanide borohydrides have not been reported yet [12].

Meanwhile, lanthanide borohydrides have seldom been introduced as polymerization catalysts, and their catalytic activity for the polymerization has not received much attention until recently. Guillaume and coworkers reported the ring-opening polymerization of ϵ -caprolactone by $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$ ($\text{Ln} = \text{La}$, Nd , Sm) [13], and studied the polymerization mechanism with $\text{Cp}_2^+\text{Sm}(\text{BH}_4)(\text{THF})$ [14]. Mountford and coworkers found that methyl methacrylate (MMA) can be polymerized by lanthanide borohydride complexes with polydentate diamide–diamide ligand [15]. Very recently, the *trans*-specific diene polymerization by $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ in the presence of MgBu_2 was also achieved [16]. These results revealed the promising future for lanthanide borohydride complexes in catalytic polymerization. It has been well recognized that the coordination ligand has great influence on the catalytic property of a complex. Hence the study on the catalytic property of

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lanthanide borohydride complexes with aryloxy ligand is interesting and important to understand the relationship between the property and the ligand.

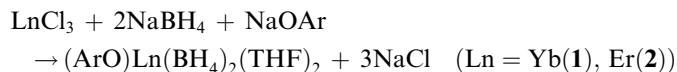
Under these consideration, we started to synthesize aryloxy lanthanide borohydrides and tested their catalytic activities for the polymerization of MMA. We found that ‘one pot’ reactions of LnCl_3 , NaBH_4 and ArONa ($\text{Ar} = \text{C}_6\text{H}_2\text{-}t\text{-Bu}_3\text{-}2,4,6$) in THF in a molar ratio of 1:3:1 in THF could afford the expected complexes (ArO)- $\text{Ln}(\text{BH}_4)_2(\text{THF})_2$ ($\text{Ln} = \text{Yb}$ (**1**), Er (**2**)). Both of the products displayed moderate high catalytic activities for the polymerization of MMA.

2. Results and discussion

2.1. Synthesis

The reaction of $\text{Ln}(\text{BH}_4)_3(\text{THF})_x$ with alkali anionic reagents is a convenient synthetic route to some lanthanide borohydride complexes. Successful examples include $[(\text{COT})\text{Nd}(\text{BH}_4)(\text{THF})_2]_2$ [11], $(\text{THF})(\text{BH}_4)_2\text{Nd}(\mu\text{-}\eta^7\text{:}\eta^7\text{-C}_7\text{H}_7)\text{Nd}(\text{BH}_4)(\text{THF})_2$ [17], $[\text{K}(18\text{-crown-}6)\{(\text{C}_{13}\text{H}_8)\text{-CPh}_2(\text{C}_5\text{H}_4)\text{Nd}(\text{BH}_4)_2\}]_2 \cdot \text{C}_4\text{H}_8\text{O}_2$ [18] and so on. We wish to synthesize $(\text{ArO})\text{Ln}(\text{BH}_4)_2(\text{THF})_x$ similarly by the reaction of $\text{Ln}(\text{BH}_4)_3(\text{THF})_x$ with ArONa . Because the aryloxy ligand has less steric bulk and lower coordination number than the traditional cyclopentadienyl ligand, the possible equilibrium between the homoleptic and heteroleptic complexes will favor the former. Hence, whether the desired complexes are stable is still a problem. Moreover, ate complex was usually obtained [10,18] by this synthetic route.

Because the synthesis of $\text{Ln}(\text{BH}_4)_3(\text{THF})_x$ has well been understood [1,4], $\text{Ln}(\text{BH}_4)_3(\text{THF})_x$ was better prepared in situ. ‘One pot’ reaction of the slurry of YbCl_3 and excess NaBH_4 with an equivalent of ArONa resulted in a red mixture at once, indicating the reaction proceeding. After the workup of procedure, red crystals of $(\text{ArO})\text{-Yb}(\text{BH}_4)_2(\text{THF})_2$ (**1**) were successfully obtained from the diethyl ether solution. This reaction was also applicable for Er element. Similar reaction of ErCl_3 , NaBH_4 and ArONa in a molar ratio of 1:3:1 in THF afforded the analogous $(\text{ArO})\text{Er}(\text{BH}_4)_2(\text{THF})_2$ (**2**).



Complexes **1** and **2** are rather sensitive to air and moisture. Diborane gas was found to release when they were exposed to moisture. However, they are thermally stable and can be stored under argon at room temperature for several months without decomposition.

2.2. Molecular structures

The solid state structures of complexes **1** and **2** were determined by the single crystal diffraction analysis. To understand more about the aryloxy ligand, the molecular structure of NaOAr was also determined. The single crystals of $[(\text{ArO})\text{Na}(\text{OEt}_2)]_2$ were obtained from the diethyl ether solution.

The crystal data and details of data collection and structure refinement of these complexes are listed in Table 1. Table 2 lists the selected bond distances and angles for **1**

Table 1
X-ray crystallographic data

Complex	1	2	$[(\text{ArO})\text{Na}(\text{OEt}_2)]_2$
Formula	$\text{C}_{26}\text{H}_{53}\text{B}_2\text{O}_3\text{Yb}$	$\text{C}_{26}\text{H}_{53}\text{B}_2\text{O}_3\text{Er}$	$\text{C}_{44}\text{H}_{78}\text{Na}_2\text{O}_4$
<i>F</i> _w	608.34	602.56	717.04
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>c</i> 2/ <i>c</i>	<i>c</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	15.613(3)	15.609(2)	9.6500(19)
<i>b</i> (Å)	13.533(2)	13.5691(19)	9.768(2)
<i>c</i> (Å)	16.076(3)	16.076(3)	12.695(3)
α (°)	90	90	102.421(6)
β (°)	116.640(5)	116.493(3)	92.529(4)
γ (°)	90	90	99.087(6)
<i>V</i> (Å ³)	3036.3(10)	3047.3(8)	1150.1(4)
<i>T</i> (K)	193(2)	193(2)	193(2)
Wavelength (Å)	0.71070	0.71070	0.71070
<i>Z</i>	4	4	1
<i>D</i> _{calc} (g/cm ³)	1.331	1.313	1.035
μ (Mo K α) (mm ⁻¹)	3.101	2.775	0.080
<i>F</i> (000)	1252	1244	396
Dimensions (mm ³)	0.50 × 0.42 × 0.11	0.37 × 0.32 × 0.23	0.61 × 0.39 × 0.20
Total reflections	14638	14499	11457
Unique reflections	2778 (<i>R</i> _{int} 0.0247)	2785 (<i>R</i> _{int} 0.0229)	4196 (<i>R</i> _{int} 0.0212)
Observed reflections	2694	2674	3503
Goodness-of-fit	1.077	1.114	1.074
<i>R</i> , <i>wR</i> (observed data)	0.0367, 0.0915	0.0352, 0.0925	0.0557, 0.1396
<i>R</i> , <i>wR</i> (all data)	0.0378, 0.0923	0.0365, 0.0937	0.0679, 0.1490

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

	1	2
<i>Bond lengths</i>		
Ln(1)–O(1)	2.042(5)	2.056(4)
Ln(1)–O(2)	2.338(5)	2.360(4)
Ln(1)–B(1)	2.460(10)	2.483(8)
O(1)–C(1)	1.351(9)	1.371(7)
<i>Bond angles</i>		
O(1)–Ln(1)–O(2)	88.53(11)	88.30(8)
O(1)–Ln(1)–O(2A)	88.53(10)	88.30(8)
O(1)–Ln(1)–B(1)	123.8(3)	123.7(3)
O(1)–Ln(1)–B(1A)	123.8(3)	123.7(2)
O(2)–Ln(1)–O(2A)	177.1(2)	176.60(16)
O(2)–Ln(1)–B(1)	92.7(3)	92.8(3)
O(2)–Ln(1)–B(1A)	89.0(3)	89.0(3)
B(1)–Ln(1)–B(1A)	112.5(7)	112.6(5)
C(1)–O(1)–Ln(1)	180.000(1)	180.000(1)

and **2**. The molecular structures of **1**, **2** and $[(\text{ArO})\text{Na}(\text{OEt}_2)_2]$ are presented in Figs. 1 and 2, respectively.

Complexes **1** and **2** are isostructural. The lanthanide atom is coordinated by an aryloxy ligand, two borohydride ligands and two THF molecules in symmetric geometry. Each complex possesses a trigonal bipyramidal structure, in which two THF ligands (O(2) and O(2A) atoms) are placed at the apical positions, and two BH_4 groups (B(1) and B(1A) atoms) and an aryloxy ligand (O(1) atom) are laid on the equatorial plane. The three atoms of O(2)–Ln(1)–O(2A) nearly lie in a line (bond angles of $177.1(2)^\circ$ and $176.60(16)^\circ$, respectively), and the Ln atom is coplanar with the B(1), B(1A) and O(1) atoms.

Complexes **1** and **2** are monomeric and unfavorable to form clusters in our experiment. However, it has been found that lanthanide borohydrides with mono-cyclopentadienyl ligand were inclined to form clusters [19]. This reflects the great effect of ligand on the structure.

The aryloxy ligand is monodentate to the lanthanide metal, different from the bridging coordination fashion in dimeric $[(\text{ArO})\text{Na}(\text{OEt}_2)_2]$. The bond distances of O(1)–

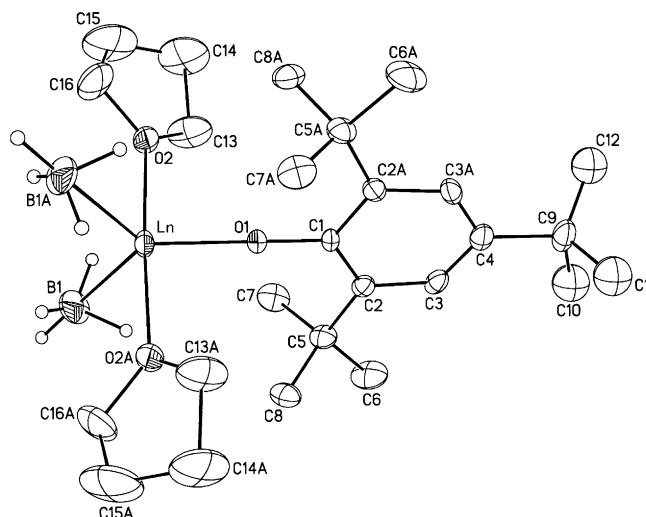


Fig. 1. Molecular structures of $(\text{ArO})\text{Ln}(\text{BH}_4)_2(\text{THF})_2$ (Ln = Yb (**1**), Er (**2**)).

C(1) (1.351(9) and 1.371(7) Å, respectively) in **1** and **2** are obviously longer than those in $[(\text{ArO})\text{Na}(\text{OEt}_2)_2]$ (1.324(2) Å), and consistent with the corresponding values in $(\text{ArO})_2\text{Yb}(\text{NPh}_2)_2\text{K}(\text{THF})_4$ (1.350(6) Å) [20] and $(\text{ArO})_2\text{Sm}(\text{N}_2\text{Ph}_2)(\text{THF})_2$ (1.359(7) Å) [21].

The most remarkable structural feature of **1** and **2** is the mode of attachment of the tetrahedral BH_4 ligands. The two boron atoms have the same ligation geometry. Each of them is attached to the metal center via three bridging hydrogen atoms. The two $\eta^3\text{-BH}_4$ ligands are located at the neighbor positions, rather than the opposite positions in $\text{Y}(\text{BH}_4)_3(\text{THF})_3$. The Yb–B distances (2.460(10) Å, 9 coordinated Yb^{3+} 1.042 Å) in **1** are comparable with the corresponding Ln– $\eta^3\text{-BH}_4$ distances in $\text{Y}(\text{BH}_4)_3(\text{THF})_3$ (2.58(1) Å, 11 coordinated Y^{3+} 1.19 Å) [4] and $[\text{K}(18\text{-crown-6})\{(\text{C}_{13}\text{H}_8)\text{CPh}_2(\text{C}_5\text{H}_4)\text{Nd}(\text{BH}_4)_2\}]_2 \cdot \text{C}_4\text{H}_8\text{O}_2$ (2.632(7) Å, 12 coordinated Nd^{3+} 1.27 Å) [18], if Shannon's ionic radii are taken into account [22]. Allowing 0.02 Å for the difference of ionic radii of Er^{3+} and Yb^{3+} , the Er–B

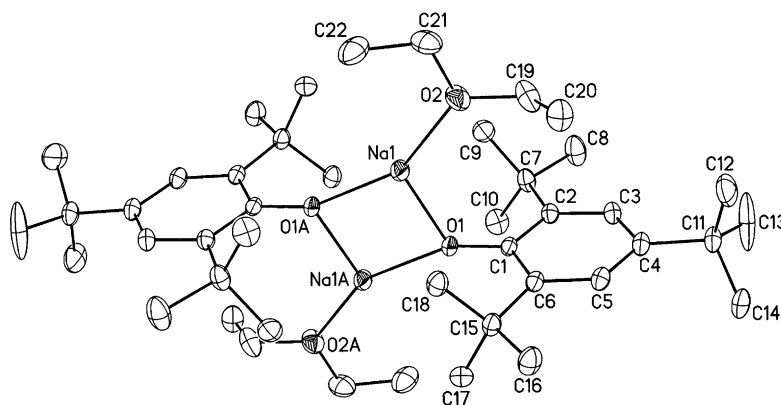


Fig. 2. Molecular structure of $[(\text{ArO})\text{Na}(\text{OEt}_2)_2]$. Selected bond distances (Å) and angles (°): Na(1)–O(1) 2.2713(14), Na(1)–O(1A) 2.1815(14), Na(1)–O(2) 2.2816(16), Na(1)–C(1) 3.0038(18), O(1)–C(1) 1.324(2), O(1A)–Na(1)–O(1) $90.35(5)^\circ$, O(1A)–Na(1)–O(2) $149.53(6)^\circ$, O(1A)–Na(1)–C(1) $114.44(5)^\circ$, O(1)–Na(1)–O(2) $119.93(6)^\circ$, O(1)–Na(1)–C(1) $24.37(4)^\circ$, C(1)–O(1)–Na(1A) $158.16(11)^\circ$, C(1)–O(1)–Na(1) $110.56(10)^\circ$, Na(1)–O(1)–Na(1A) $89.65(5)^\circ$.

distances (2.483(8) Å) in **2** are comparable with those in **1**. These Ln–B distances in **1** and **2** are greatly shorter than the corresponding Ln– η^2 -BH₄ distances in Y(BH₄)₃(THF)₃ (2.68(2) Å) and (CH₃OCH₂CH₂C₉H₆)₂Y(BH₄) (2.693(8) Å) [9]. The short distances are characteristics of tridentate BH₄ ligands.

In the solid state of [(ArO)Na(OEt₂)]₂, four atoms of Na(1)–O(1)–Na(1A)–O(1A) lie in a plane. The Na(1)–O(1) and Na(1)–O(1A) bonds are inequivalent. The shape of Na(1)–O(1)–Na(1A)–O(1A) plane is nearly a rectangle. Two phenyl ring planes are vertical to the Na(1)–O(1)–Na(1A)–O(1A) plane, but each inclines to a sodium atom. The Na(1)–C(1) distance is 3.0038(18) Å. This distance is greatly shorter than the sum of van der Waals radii of carbon atom (1.85 Å) and sodium atom (2.31 Å). It means that Na–C(arene) close interaction exists in the dimeric complex.

2.3. Polymerization activity

Lanthanide borohydride complexes have seldom been introduced as polymerization catalysts. Although several recent reports have touched this area, their catalytic activity for the polymerization has not well been evaluated. We found that both of **1** and **2** can catalyze the polymerization of methyl methacrylate in moderate high catalytic activities. Detailed polymerization results were listed in Table 3.

Although the catalytic activities of **1** and **2** are not good enough when compared with those of alkyl [2] and amido [3] lanthanocenes, the catalytic behavior has its own feature, especially on the effect of polymerization temperature. For complex **1**, as temperature rose from 0 to 25 °C, the yield of polymer decreased from 60.1% (run 5) to 13.1% (run 7). It nearly could not catalyze the polymerization at above 40 °C. However, as temperature decreased below 0 °C, the polymerization activity did not increase any more.

At –30 °C, the catalysts had no reactivity to the monomers and could be recovered from the system. We supposed, on the one hand, the initiation reaction required certain activation energy. On the other hand, side reactions would be inevitable at elevated temperature. The two contrary effects resulted in the occurrence of the optimum temperature. This phenomenon was quite different from the unique pioneering report of [Sm(N₂NN^{TMS})BH₄]₂ [N₂NN^{TMS} = (2-C₅H₄N)CH₂N(CH₂CH₂NSiMe₃)₂] [15]. Complex [Sm(N₂NN^{TMS})BH₄]₂ still showed catalytic activity at –78 °C. As [Sm(N₂NN^{TMS})BH₄]₂ contains two Ln–N active bonds simultaneously [3], we are not clear whether this reactivity at low temperature comes from the BH₄ group. The stereoregularity analysis showed that the PMMA was mainly syndiotactic (ca. 60%). The content of isotactic part was about 6%. The tacticity of polymers varied little as the polymerization temperature and time changed.

The polymerization character of the Er complex was similar to that of the Yb complex. Complexes **1** and **2** displayed comparable catalytic activities for the polymerization of MMA.

3. Conclusions

We have successfully synthesized the first aryloxy lanthanide borohydrides. The structures of (ArO)Ln(BH₄)₂-(THF)₂ (Ln = Yb (**1**), Er (**2**)) were elucidated. We have also described their catalytic behavior for the polymerization of MMA. These results reveal that aryloxy ligand has great influence on the catalytic property of a lanthanide borohydride complex and lanthanide borohydride systems have considerable scope for development. Further studies on lanthanide borohydride complexes with other ligands are in progress and will be reported in due course.

Table 3
Polymerization of MMA by **1** and **2**

Run	Catalyst	Temperature (°C)	Time (h)	Yield (%)	Molecular weight (×10 ⁴)	Tacticity (%)		
						<i>rr</i>	<i>mr</i>	<i>mm</i>
1	1	–30	1.0	0	–	–	–	–
2	1	–10	1.5	47.1	9.80	59.5	33.6	6.9
3	1	0	0.5	36.7	6.84	60.6	34.0	5.4
4	1	0	1.0	49.1	6.96	59.4	34.6	6.0
5	1	0	1.5	60.1	8.34	59.2	34.0	6.8
6	1	10	2.0	51.3	7.64	60.1	34.1	5.8
7	1	25	3.0	13.1	–	–	–	–
8	1	40	5.0	5.4	–	–	–	–
9	2	–30	1.0	0	–	–	–	–
10	2	–10	1.5	41.3	9.65	63.4	31.5	5.1
11	2	0	0.5	32.5	5.08	60.1	34.3	5.6
12	2	0	1.0	49.2	5.07	60.7	34.3	5.0
13	2	0	1.5	57.5	6.97	60.0	34.5	5.5
14	2	10	2.0	50.5	5.06	60.6	33.8	5.6
15	2	25	3.0	14.3	–	–	–	–
16	2	40	5.0	5.7	–	–	–	–

Polymerization conditions: *n* (MMA/Ln) = 200 (mol. ratio), [MMA] = 4.644 mol/L, solvent = toluene.

4. Experimental

4.1. General procedure

All manipulations were carried out under an atmosphere of argon using Schlenk techniques. Tetrahydrofuran (THF), toluene and diethyl ether (OEt₂) were distilled from sodium/benzophenone ketyl. Sodium 2,4,6-tri-*tert*-butylphenolate (NaOAr) was prepared from metallic sodium and 2,4,6-tri-*tert*-butylphenol (Acros reagent) in THF. Carbon and hydrogen elemental analyses were carried out by using an EA1110-CHNSO elemental analyzer. Lanthanide metal analysis was carried out by complexometric titration. Melting point was measured in a sealed Ar-filled capillary and uncorrected. MMA was dried over CaH₂ and distilled. The molecular weight of polymers was calculated according to the intrinsic viscosity, determined by a viscosity detector. The microstructure of PMMA was determined by its ¹H NMR spectrum, which was obtained by using a Unity Inova-400 spectrometer.

4.2. Synthesis of (ArO)Yb(BH₄)₂(THF)₂ (**1**)

A flask was charged with YbCl₃ (0.57 g, 2.04 mmol) and excess NaBH₄ (0.31 g, 8.20 mmol), and THF (about 20 mL) was condensed in. The reaction mixture was stirred at room temperature for 24 h. To the white slurry of above mixture was added the THF solution of ArONa (about 3.3 mL, 2.04 mmol) with a syringe. The reaction mixture became red at once. After being stirred at room temperature for another 48 h, the mixture was evaporated under vacuum. The residue was extracted with diethyl ether and centrifugalized to separate the NaCl and excess NaBH₄. The red clear solution was concentrated and kept at -20 °C. Red crystals of **1** (0.41 g, 0.67 mmol, 32.8%) were produced. M.p.(dec.): 116 °C. Anal. Found: C, 51.12; H, 8.72; Yb, 28.31. Calc. for C₂₆H₅₃B₂O₃Yb: C, 51.33; H, 8.78; Yb, 28.44%. IR (cm⁻¹): 2958(s), 2382(w), 2294(m), 2228(w), 1635(m), 1436(s), 1364(s), 1236(s), 1161(s), 1124(s), 998(br,m), 810(w).

4.3. Synthesis of (ArO)Er(BH₄)₂(THF)₂ (**2**)

The procedure followed was similar to that for **1**. Complex **2** was obtained as pink crystals in a 28.6% yield. M.p.(dec.): 181 °C. Anal. Found: C, 51.76; H, 8.82; Er, 27.66. Calc. for C₂₆H₅₃B₂O₃Er: C, 51.82; H, 8.86; Er, 27.75%. IR (cm⁻¹): 2958(s), 2384(w), 2294(m), 2228(w), 1634(m), 1436(s), 1364(s), 1236(s), 1161(s), 1123(s), 1022(br,m), 810(w), 765(w), 718(w).

4.4. X-ray structure determination for **1** and **2**

A red crystal **1** of dimensions 0.50 × 0.42 × 0.11 mm³ was sealed in a thin walled glass capillary under argon and placed in the cold nitrogen stream of a Rigaku Mercury CCD diffractometer. Data were collected by use of

the ω -2 θ scan technique with Mo K α radiation ($\lambda = 0.71070 \text{ \AA}$). All data were corrected for Lorentz and polarization effect, and the structure was solved by direct method. The hydrogen atoms were located and refined from geometric consideration. The non-hydrogen atoms were refined anisotropically. All calculations were performed using SHELXS-97 and SHELXL-97 program packages [23].

The solution of structure for **2** is similar to that of **1**. Crystallographic details of **1** and **2** are listed in Table 1.

4.5. Polymerization reaction

A flask equipped with a magnetic stirring bar, to which were added the catalyst and toluene solvent, was then placed in a thermostatic bath. After some time, the monomer was added into the flask using a syringe. The contents of the flask were stirred for a determined time. The reaction was quenched by addition of ethanol containing hydrochloric acid. The polymer was washed with ethanol containing acid, dried under vacuum at 45 °C and weighed.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 260692 for complex **1**, CCDC No. 279958 for complex **2** and CCDC No. 260693 for [(ArO)-Na(OEt₂)₂]₂. Copies of these information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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