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Synthesis of bis(methylcyclopentadienyl)(piperidino)lanthanoids and their catalytic behavior for polymerization of methyl methacrylate

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Abstract

Reaction of anhydrous $LnCl_3$ with MeC_5H_4Na, followed by the treatment with $LiNC_5H_{10}$ in toluene at 0°C, affords the neutral amido complexes $(MeC_5H_4)_2LnNC_5H_{10}(HNC_5H_{10})$ (Ln = Yb (**1**), Er (**2**), Y (**3**)). The X-ray analysis determined the crystal structure of **2**. All of these complexes exhibit good catalytic activity for the polymerization of methyl methacrylate. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Synthesis; X-ray structure; MMA polymerization; Lanthanocene amides

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1. Introduction

In recent years, the use of lanthanoids as single-component catalysts in polymer synthesis has attracted a great deal of attention. Organolanthanoid complexes such as Cp^*_2LnR ($Cp^* = \eta^5$-C_5Me_5, R = alkyl and hydride) have been found to be highly active catalysts for the polymerization of ethylene [1], methyl methacrylate (MMA) [2] and alkyl acrylates [3], as well as the ring opening polymerization of lactones ([2]C, [4]). Homoleptic lanthanoid alkoxide and thiolate compounds can also initiate the polymerization of polar monomers [5–11]. Besides, divalent lanthanoid complexes based initiators for the polymerization of MMA ([2]b), ε-caprolactone [12] and for the copolymerization of ethylene carbonate and ε-caprolactone [13], have been demonstrated.

In contrast, the utilization of organolanthanoid amides as homogeneous catalysts for the polymerization of polar vinyl monomers remains relatively unexplored [14]. Like lanthanocene hydride and alkyl compounds, in fact, lanthanocene amides also exhibit high reactivity in the hydroamination/cyclization of aminoalkenes [15] and in the polymerization of MMA [14]. Our recent studies have shown that (diisopropylamido)bis(methylcyclopentadienyl)lanthanoids can be active catalysts for the polymerization of phenyl isocyanate [16] and MMA [17]. In order to further investigate the effect of amido ligands around central metals on catalytic activity, we synthesized bis(methylcyclopentadienyl)(piperidino)lanthanoids and determined the X-ray crystal structure of the erbium complex. Furthermore, their catalytic behavior for the polymerization of MMA was tested. Now, we would like to report the results of these studies.

2. Results and discussion

2.1. Synthesis of $(MeC_5H_4)_2LnNC_5H_{10}(HNC_5H_{10})$ (Ln = Yb (**1**), Er (**2**), Y (**3**))

Organolanthanoid amides were prepared by two main routes: (1) the ionic metathesis of alkali metal amides with lanthanocene chlorides [18–25]; (2) the metalation of various amines by lanthanocene alkyl or

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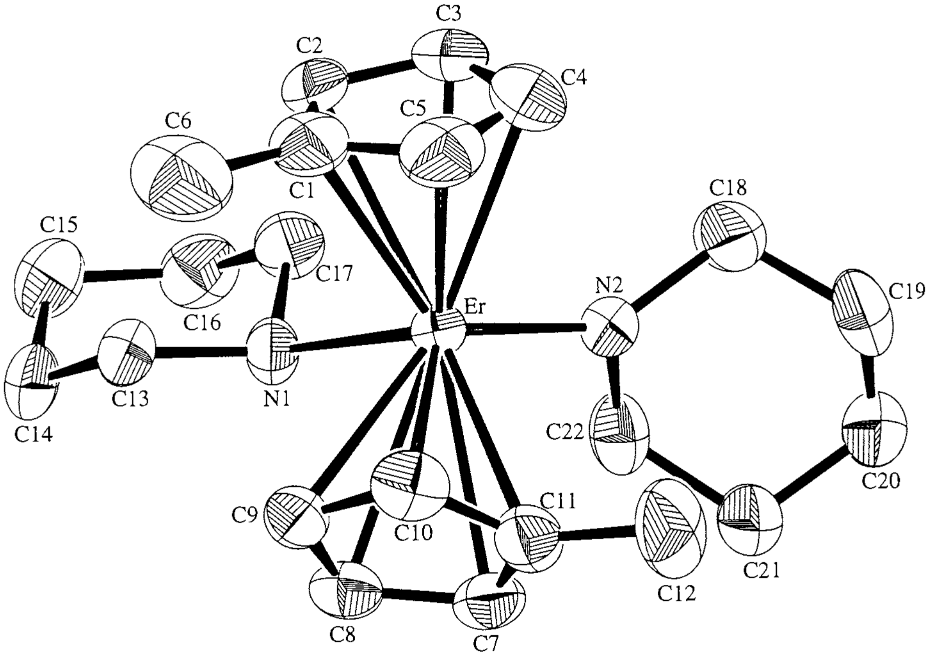

Fig. 1. Crystal structure of complex **2**.

hydride precursors [15,22,26–28]. The neutral and ionic organolanthanoid complexes with $N(SiMe_3)_2$ [21–25,29], NPh_2 [28,30–33], NMe_2 [26,27], and NH_2 [18,26,34,35] as ligands have been published. Recently, we succeeded in preparing the desired neutral (diisopropylamido)bis(methylcyclopentadienyl)lanthanoids by the ionic metathesis route [16]. The results prompted us to try the synthesis of other lanthanoid derivatives with different amido ligands using the same method. When $LnCl_3$ reacts with two equivalents of MeC_5H_4Na in THF, followed by the treatment with $LiNC_5H_{10}$ in toluene at 0°C, the neutral amido complexes have been obtained as crystals, as shown in the following equations:

$$LnCl_3 + 2MeC_5H_4Na \xrightarrow{THF} (MeC_5H_4)_2LnCl(THF) + NaCl$$

$$(MeC_5H_4)_2LnCl(THF) + LiNC_5H_{10} \xrightarrow{toluene\ (0^{\circ}C)} (MeC_5H_4)_2LnNC_5H_{10}(HNC_5H_{10}) + LiCl$$

Complexes **1**–**3** were characterized by elemental analysis, IR, ^1H-NMR (for **3**), and MS. The X-ray analysis determined the crystal structure of **2**. These compounds are highly soluble in THF and DME, moderately soluble in diethyl ether and aromatic solvents, and insoluble in aliphatic hydrocarbons and are extremely air- and moisture-sensitive. Their melting points are around 110°C.

All of these complexes contain the coordinated piperidine instead of expected THF molecules. This may be due to the use of excess piperidine in the preparation of lithium amide. In addition, the coordinated piperidine is not easily removed by recrystallization from diethyl ether or by prolonged pumping under dynamic vacuum.

2.2. *X-ray crystal structure of* **2**

To our knowledge, the X-ray structural analyses of the neutral lanthanoid amides with the less bulky methylcyclopentadienyl as auxiliary ligands are still scant [34]. Therefore, the determination of the crystal structure of the complex **2** was desirable.

As shown in Fig. 1, the molecule has a monomeric structure in which the erbium ion is coordinated to the two methylcyclopentadienyl rings and two nitrogen atoms from the piperidino group and piperidine molecule in a distorted tetrahedral geometry. The formal coordination number of the central metal is eight. Selected bond distances and angles were given in Table 1.

In complex **2**, the Er–N(I) and Er–N(2) distances are 2.464(7) and 2.159(8) Å, respectively. The large disparity (ca. 0.3 Å) in the Er–N bond lengths shows that their bonding modes are different. It was reported that a typical $R_3N{:}\rightarrow Y$ donor bond distance ranges from 2.47 to 2.63 Å [36]. Thus, the $R_3N{:}\rightarrow Er$ donor bond distance was estimated to be in the range of 2.455 to 2.615 Å after the subtraction of the difference (ca. 0.015 Å) [37] in ionic radii for eight-coordinate Er^{3+} and Y^{3+}. Obviously, the present Er–N(1) distance falls within the range of a donor bond.

The Er–N(2) distance is ca. 0.1 Å shorter than those in previously characterized lanthanoid amido com-

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

Bond distances (Å)			
Er–N(1)	2.464(7)	Er–N(2)	2.159(8)
Er–C(1)	2.664(9)	Er–C(2)	2.664(8)
Er–C(3)	2.664(8)	Er–C(4)	2.63(1)
Er–C(5)	2.651(10)	Er–C(7)	2.712(7)
Er–C(8)	2.708(8)	Er–C(9)	2.684(8)
Er–C(10)	2.664(9)	Er–C(11)	2.702(8)
Er–Cent(1)[a]	2.377	Er–Cent(2)[a]	2.416
Bond angles (°)			
N(1)–Er–N(2)	93.0(2)	Cent(1)–Er–Cent(2)	126.3
Cent(1)–Er–N(1)	106.9	Cent(1)–Er–N(2)	109.6
Cent(2)–Er–N(1)	102.5	Cent(2)–Er–N(2)	112.7
Er–N(I)–C(13)	116.0(5)	Er–N(I)–C(17)	114.6(5)
Er–N(2)–C(22)	118.3(5)	Er–N(2)–C(18)	134.3(7)

[a] Cent(1) is the centroid of the C(1)–C(5) ring and Cent(2) is the centroid of the C(7)–C(11) ring.

plexes ($(C_5Me_5)_2YN(SiMe_3)_2$: 2.274(5) Å [21]; $[(CH_3C_5H_4)_2YbNH_2]_2$: 2.31 Å [34]; $(C_5Me_5)_2SmN(SiMe_3)_2$: 2.301(3) Å [23]; $(C_5H_5)_2Lu(NC_4H_2Me_2)(THF)$: 2.289(4) Å [20]) even if corrections are made for trivalent eight-coordinate ionic radii. However, the Er–N(2) distance is comparable to 2.313(10) Å in the similar complex $(C_5Me_5)_2LaNHCH_3(NH_2CH_3)$ [15]] when the 0.1 56 Å difference [37] in radial size is considered. Comparison of the Er–N(2) distance can also be made with 2.353(4) Å in the highly unsaturated mono(pentamethylcyclopentadienyl) cerium complex: $(C_5Me_5)Ce[N(SiMe_3)_2]_2$ [38].

The Er–C(ring) distances range from 2.63(1) to 2.712(7) Å. The average Er–C(ring) distance of 2.674 Å is on the long end of the range observed in other trivalent erbium complexes: $[(C_5H_5)_2ErCl]_2$, 2.59 Å [39]; $[(MeOCH_2CH_2C_5H_4)_2Er(\mu\text{-}OH)]_2$, 2.68 Å [40]; $[(C_5H_5)_2ErC{\equiv}C(t\text{-}Bu)]_2$, 2.62 Å [41]; $\{(C_5H_5)_2Er[\mu,\eta\text{-}(HC{=}N(t\text{-}Bu))]\}_2$, 2.645(7) Å [36]; $(C_5H_5)_2Er(\mu\text{-}Me)_2Li(tmed)$, 2.641(11) Å [42]. The (ring centroid)–Er–(ring centroid) angle in complex **2**, 126.3°, is much larger than the angle N(1)–Er–N(2) 93.0(2)° and shows the large deviation from the ideal tetrahedral geometry. This behavior is not unusual and has been observed in the similar complex $(C_5Me_5)_2LaNHCH_3(NH_2CH_3)$, (ring centroid)–La(1)–(ring centroid) 136.3(4)°, (ring centroid)La(2)–(ring centroid) 140.8(4)°, N(1)–La(1)–N(2) 95.4(3)°, N(3)–La(2)–N(4) 92.4(3)° [15].

2.3. Catalytic behavior

On the basis of well-defined structures of these complexes, we tested their catalytic behavior for the polymerization of MMA.

It can be seen from Table 2 that complexes **1**–**3** all give satisfying polymerization yields at 0°C for 2 h in the case of 0.2 mol% catalyst concentrations. However, different catalytic activity among lanthanoid analogues has been noticed. The observed order, Yb > Er > Y, is contrary to the increasing order of ionic radii, Yb(0.985) < Er(1.004) < Y(1.019 Å) [37], that is to say, the activity decreases with an increase of ionic radii of the central metal. The results are completely different from those reported on the polymerization of MMA using (diisopropylamido)bis(methylcyclopentadienyl)-lanthanoids and lanthanocene hydride or alkyl compounds as catalysts, in which the activity increases with increasing ionic radii of the metal elements ([2]b, [17]). The real reason is not clear yet and further study is in progress.

Table 2 also lists the results of MMA polymerization using complex **1** at various catalyst concentrations. The polymerization gives quantitative yields and narrow molecular weight distribution (MWD) at 0°C for 2 h in the case of 0.2 and even 0.07 mol%. However, the yield

Table 2
Polymerization of MMA with $(MeC_5H_4)_2LnNC_5H_{10}(HNC_5H_{10})$

Entry	Catalyst	Catalyst concentration (mol%)	Temperature (°C)	Yield (%)	10^{-3} M_n	M_w/M_n	Tacticity (%)	
							rr	*rm*
1	1	0.2	40	85.5	146	2.14	76.5	23.5
2	1	0.2	25	95.8	198	2.02	78.7	21.3
3	1	0.2	0	100	125	1.14	80.5	19.5
4	1	0.2	−78	100	229	1.11	87.1	12.9
5	1	0.07	0	100	293	1.16		
6	1	0.05	0	43.7	583	1.78		
7	2	0.2	0	98.1	263	3.27		
8	2	0.07	0	89.3				
9	3	0.2	0	94.0	220	3.74		
10	3	0.07	0	81.7				

Reaction condition: solvent, toluene; solvent/$[MMA]_0 = 10$ vol/vol; time, 2 h.

decreases to 43.7% and the MWD slightly broadens when the catalyst amount is further lowered to 0.05 mol%. In combination with the results obtained in the polymerization of MMA with $(MeC_5H_4)_2LnN(^iPr)_2$ (THF) (Ln = Yb (**4**), Er (**5**), Y (**6**)) [17], the catalytic activity of these different amido complexes can be lined in the following order: $6 > 5 > 4$ ca. $1 > 2 > 3$. Furthermore, all of these amido complexes exhibit much higher activity than that of the chiral organolanthanoid amide (*R*)-(neomenthyl)$LaN(TMS)_2$ [14]. This is presumably related to the steric encumbrance and operational nucleophilicity of amido group around the central metal.

The effect of temperature on polymerization reactions was also investigated. Table 2 reveals a decline in polymer yield and the broadening of the molecular weight distribution with increasing reaction temperature. This may be caused by thermally-activated side reactions, which inhibited the polymerization reaction. In addition, the stereoregularity of resulting polymer varies greatly depending on the polymerization temperature. Table 2 indicates that the syndiotacticity increased from 76.5 to 87.1% when the temperature is changed from 40 to − 78°C. This is in line with the general trend observed in MMA polymerizations.

3. Experimental section

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. THF, toluene, and diethyl ether were dried and freed of oxygen by refluxing over Na or sodium benzophenone ketyl and distilled under argon prior to use. MMA was distilled over fresh calcium hydride powder and stored over molecular sieves 3A under argon. Anhydrous $LnCl_3$ was made according to the published method [43]. $LiNC_5H_{10}$ was obtained by the reaction of HNC_5H_{10} with *n*-BuLi in a solution of THF and hexane.

Melting points were determined in sealed argon-filled capillaries and were uncorrected. Metal analyses was carried out by complexometric titration. Carbon, hydrogen and nitrogen analyses was carried out by direct combustion. The IR spectra were recorded on a Magna-550 spectrometer. ^1H and ^{13}C-NMR spectra were obtained with a Bruker AM-300 apparatus. Electron ionization mass spectra (EI-MS) were determined on a HP5989A spectrometer. The number-average molecular weights (M_n) and the molecular weight distribution (M_w/M_n) were determined by GPC (gel permeation chromatography) using a Waters 150C module equipped with two Ultrastyragel 103 Å and linear columns at 25°C. Molecular weight data was obtained versus monodisperse polystyrene calibration samples. THF was used as the eluent.

3.1. Preparation of $(MeC_5H_4)_2YbNC_5H_{10}(HNC_5H_{10})$ **1**

To a slurry of $YbCl_3$ (3.19 g, 11.42 mmol) in 20 ml THF, 18.51 ml of a solution of MeC_5H_4Na (22.84 mmol) in THF was added. The mixture was stirred at room temperature (r.t.) for 48 h. After centrifugation, the THF was completely removed and the oily residue was extracted with 50 ml toluene. The toluene extracts (49 ml, 8.96 mmol) were then cooled to 0°C and 20 ml of a solution of $LiNC_5H_{10}$ (8.96 mmol) in toluene was added from a syringe. The mixture was stirred for 1 h at 0°C and then for another 48 h at r.t. After centrifugation, the toluene was pumped off and the solids were extracted with diethyl ether. When the extracts were concentrated and cooled to − 10°C, dark crystals were formed. Yield 2.51 g (43.9%). M.p. = 112–114°C. Anal. Calc. for $C_{22}H_{35}N_2Yb$: C, 52.51; H, 7.24; N, 5.62; Yb, 34.40. Found: C, 52.78; H, 7.06; N, 5.59; Yb, 34.57%. IR (KBr pellet, cm^{-1}): 3445(s), 3426(s), 2932(s), 2855(m), 2739(w), 1698(w), 1624(m), 1528(s), 1501(s), 1443(s), 1296(s), 1258(m), 1111(w), 1049(w), 860(w), 802(m), 733(m), 675(m), 648(m), 559(m). EI-MS (70 eV): *m/e* (%) 415 (35, $M^+-HNC_5H_{10}$), 332 (65, $M^+-HNC_5H_{10}-NC_5H_{10}$), 253 (40, $M^+-HNC_5H_{10}-NC_5H_{10}-MeC_5H_4$), 79 (100).

3.2. Preparation of $(MeC_5H_4)_2ErNC_5H_{10}(HNC_5H_{10})$ **2**

This compound was prepared from 3.18 g of $ErCl_3$ (11.62 mmol), 23.24 mmol of MeC_5H_4Na, 20 ml of a solution of $LiNC_5H_{10}$ (9.52 mmol) in toluene using the procedure described above. Pink crystals were obtained. Yield 2.35 g (40.9%). M.p. = 109–110°C. Anal. Calc. for $C_{22}H_{35}N_2Er$: C, 53.01; H, 7.34; N, 5.88; Er, 33.56. Found: C, 53.40; H, 7.14; N, 5.66; Er, 33.80%. IR (KBr pellet, cm^{-1}): 3453(m), 3067(w), 2932(s), 2855(m), 2735(w), 1632(w), 1528(s), 1493(s), 1443(s), 1292(s), 1258(m), 1110(w), 1030(w), 870(w), 800(w), 760(w), 670(m), 620(m), 563(m). EI-MS (70 eV): *m/e* (%) 325 (45, $M^+-HNC_5H_{10}-NC_5H_{10}$), 246 (10, $M^+-HNC_5H_{10}-NC_5H_{10}-MeC_5H_4$), 79 (100).

3.3. Preparation of $(MeC_5H_4)_2YNC_5H_{10}(HNC_5H_{10})$ **3**

This complex was prepared from 3.30 g of YCl_3 (16.90 mmol), 33.80 mmol of MeC_5H_4Na, 20 ml of a solution of $LiNC_5H_{10}$ (13.38 mmol) in toluene using the procedure described above. Colorless crystals were isolated. Yield 2.68 g (38.2%). M.p. = 106–109°C. Anal. Calc. for $C_{22}H_{35}N_2Y$: C, 63.12; H, 8.97; N, 6.49; Y, 21.21. Found: C, 63.44; H, 8.49; N, 6.72; Y, 21.35%. IR (KBr pellet, cm^{-1}): 3484(m), 2932(s), 2855(m), 2735(w), 1644(w), 1528(s), 1497(s), 1443(s), 1392(s), 1258(m), 1111 (w), 1030(m), 864(m), 800(w), 756(w), 613(m), 563(m). ^1H-NMR (C_6D_6, 300 MHz, 25°C): $\delta = 1.22$–1.65 (m, 12H, NC_5H_{10}); 2.33–2.40 (m, 6H, MeC_5H_4);

Table 3
Crystallographic data for 2

Empirical formula	$C_{22}H_{35}N_2Er$
Molecular weight	494.79
Crystal color, habit	Pink, prismatic
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)
a (Å)	13.547(8)
b (Å)	17.806(4)
c (Å)	9.130(3)
V (Å^3)	2202(1)
Z	4
$D_{\mathrm{calc.}}$ (g. cm^{-3})	1.492
μ (Mo–K$_\alpha$) (cm^{-1})	38.10
2 θ range for data collection (°)	18.8–25.5
F(000)	996.00
Scan type	ω-2 θ
Scan width	(1.78 + 0.30 tan θ)
Measured reflections	2881
Unique reflections with $I > 3.00\sigma(I)$	2503
Number of variables	227
Final R, Rw	0.030, 0.039

$R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $Rw = [(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)]^{\frac{1}{2}}$.

Table 4
Atomic coordinates and isotropic displacement coefficients for **2**

Atom	x	y	z	$B_{\mathrm{eq}}(A^2)$
Er	0.04842(3)	0.07964(2)	0.14066(4)	3.445(7)
N(1)	0.1864(5)	0.1401(4)	0.2711(7)	3.9(1)
N(2)	−0.0267(5)	0.0505(4)	0.3414(9)	4.4(2)
C(1)	0.0224(8)	0.1807(6)'	−0.071(1)	5.6(2)
C(2)	0.0194(7)	0.2212(5)	0.056(1)	5.0(2)
C(3)	−0.0656(7)	0.2015(5)	0.132(2)	6.1(3)
C(4)	−0.1137(8)	0.1468(7)	0.053(2)	7.4(3)
C(5)	−0.0612(9)	0.1332(6)	−0.076(1)	6.3(3)
C(6)	0.096(1)	0.1912(9)	−0.191(2)	9.0(4)
C(7)	0.1198(7)	−0.0626(4)	0.135(1)	4.7(2)
C(8)	0.2003(7)	−0.0166(5)	0.096(1)	4.5(2)
C(9)	0.1793(7)	0.0157(5)	−0.0414(10)	4.2(2)
C(10)	0.0865(8)	−0.0113(5)	−0.084(1)	4.8(2)
C(11)	0.0504(8)	−0.0602(5)	0.026(1)	5.1(2)
C(12)	−0.0459(9)	−0.1022(7)	0.020(2)	8.1(3)
C(13)	0.2647(7)	0.1739(5)	0.177(1)	4.6(2)
C(14)	0.3524(7)	0.2014(5)	0.263(1)	5.2(2)
C(I5)	0.3215(8)	0.2569(5)	0.375(1)	6.0(2)
C(16)	0.2401(9)	0.2251(5)	0.474(1)	5.7(2)
C(17)	0.1557(7)	0.1970(5)	0.384(1)	4.7(2)
C(18)	−0.1285(9)	0.0610(6)	0.397(1)	6.9(3)
C(19)	−0 1781(8)	−0.0128(8)	0.431(2)	7.8(4)
C(20)	−0.1209(9)	−0.0562(6)	0.545(2)	7.2(3)
C(21)	−0.0140(8)	−0.0639(6)	0.498(1)	6.2(3)
C(22)	0.0286(7)	0.0120(6)	0.454(1)	5.1(2)

$B_{\mathrm{eq}} = 8\pi^2/3(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

2.47 (s, 1H, HNC_5H_{10}); 2.64 (s, 8H, NC_5H_{10}); 6.00–6.14 (m, 8H, MeC_5H_4). EI-MS (70 eV): m/e (%) 247 (100, M^+–HNC_5H_{10}–NC_5H_{10}), 167 (20, M^+–HNC_5H_{10}–NC_5H_{10}–MeC_5H_4).

3.4. Typical experiment for polymerization of MMA

To a toluene solution (12 ml) of MMA (15.97 mmol, 1.70 ml) was added at once the toluene solution (5 ml) of $(MeC_5H_4)_2YbNC_5H_{10}(HNC_5H_{10})$ (0.0320 mmol, 16 mg) with vigorous magnetic stirring at the desired temperature. After the polymerization was held for 2 h, the viscous solution was poured into ethanol containing 5% HCI solution (l00 ml) to induce the precipitation of the polymer. The resulting polymer was washed three times with ethanol and dried in vacuum at 50°C.

3.5. X-ray crystallographic analysis of **2**

A pink crystal of approximate dimensions 0.20 × 0.20 × 0.30 mm was mounted in a thin walled glass capillary for X-ray structure analysis. The data were collected at r.t. on a Rigaku AFC7R diffractometer using graphite monochromated Mo–K$_\alpha$ ($\lambda = 0.71069$ Å) radiation. During the period of collection of the intensity data, no significant decays were observed. The intensity was corrected for Lorentz-polarization effects and empirical absorption. A summary of crystallographic data is given in Table 3. Atomic coordinates and isotropic displacement coefficients were listed in Table 4.

The structure was solved by the heavy-atom method. The coordinates of the Er atom derived from Patterson analysis were used to calculate the Fourier map. Successive Fourier syntheses gave the coordinates of all non-hydrogen atoms refined by the block-diagonal least-squares method. H atoms were placed in calculated positions and assigned isotropic thermal parameters. Further refinement led to final convergence at $R = 0.030$. All calculations were performed on an IRIS INDIGO computer using DIRDIF92 programs.

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References

[1] (a) G. Jeske, H. Mauermann, P.N. Swepston, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8091. (b) P.L. Watson, D.C. Roe, J. Am. Chem. Soc. 104 (1982) 6471. (c) P.L. Watson, G.W. Parshall, Acc. Chem. Res. 18 (1985) 51. (d) W.J. Evans, D.M. DeCoster, J. Greaves, Organometallics 15 (1996) 3210.

[2] (a) H. Yasuda, Y. Yamamoto, K. Yokota, S. Miyake, A. Nakamura, J. Am. Chem. Soc. 114 (1992) 4908. (b) H. Yasuda, Y. Yamamoto, M. Yamashita, et al., Macromolecules 26 (1993) 7134. (c) L.S. Boffa, B.M. Novak, Macromolecules 27 (1994) 6993.

[3] E. Ihara, M. Morimoto, H. Yasuda, Macromolecules 28 (1995) 7886.
[4] M. Yamashita, Y. Takemoto, E. Ihara, H. Yasuda, Macromolecules 29 (1996) 1798.
[5] R. Nomura, T. Toneri, T. Endo, Polym. Prepr. Jpn 34 (1994) 156.
[6] S.J. McLain, T.M. Ford, N.E. Drysdale, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 33 (1992) 463.
[7] S.J. McLain, N.E. Drysdale, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 33 (1992) 174.
[8] S.J. McLain, T.M. Ford, N.E. Drysdale, J.L. Shreeve, W.J. Evans, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 35 (1994) 534.
[9] N. Fukuwatari, H. Sugimoto, S. Inoue, Polym. Prepr. Jpn. 43 (1994) 154.
[10] Y. Shen, Z. Shen, F. Zhang, Y. Zhang, Polym. J. 27 (1995) 59.
[11] Y. Nakayama, T. Shibahara, H. Fukumoto, A. Nakamura, K. Mashima, Macromolecules 29 (1996) 8014.
[12] W.J. Evans, H. Katsumata, Macromolecules 27 (1994) 2330.
[13] W.J. Evans, H. Katsumata, Macromolecules 27 (1994) 4011.
[14] M.A. Giardello, Y. Yamamoto, L. Brard, T.J. Marks, J. Am. Chem. Soc. 11 (7) (1995) 3276.
[15] M.R. Gagne, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 275.
[16] L. Mao, Q. Shen, M. Xue, J. Sun, Organometallics 16 (1997) 3711.
[17] L. Mao, Q. Shen, J. Polym. Sci. Part A: Polym. Chem. (in press).
[18] R.E. Maginn, S. Marastyrskyj, M. Dubeck, J. Am. Chem. Soc. 85 (1963) 672.
[19] H. Schumann, P.R. Lee, J. Loebel, Chem. Ber. 122 (1989) 1897.
[20] H. Schumann, P.R. Lee, A. Dietrich, Chem. Ber. 123 (1990) 1331.
[21] K.H. den Haan, J.L. de Boer, J.H. Teuben, et al., Organometallics 5 (1986) 1726.
[22] H.J. Heeres, J. Renkema, M. Booij, A. Meetsma, J.H. Teuben, Organometallics 7 (1988) 2495.
[23] W.J. Evans, R.A. Keyer, J.W. Ziller, Organometallics 12 (1993) 2618.
[24] T.D. Tilley, R.A. Andersen, Inorg. Chem. 20 (1981) 3267.
[25] M. Booij, N.H. Kiers, H.J. Heeres, J.H. Teuben, J. Organomet. Chem. 364 (1989) 79.
[26] J.E. Bercaw, D.L. Davies, P.T. Wolczanski, Organometallics 5 (1986) 443.
[27] S.P. Nolan, D. Stern, T.J. Marks, J. Am. Chem. Soc. 111 (1989) 7844.
[28] H. Schumann, E. Palamidis, J. Loebel, J. Organomet. Chem. 390 (1990) 45.
[29] M.A. Giardello, V.P. Conticello, L. Brard, et al., J. Am. Chem. Soc. 116 (1994) 10212.
[30] L. Mao, Q. Shen, S. Jin, Polyhedron 13 (1994) 1023.
[31] J. Guan, S. Jin, Y. Lin, Q. Shen, Organometallics 11 (1992) 2483.
[32] L. Mao, Q. Shen, Y. Lin, Youji Huaxue 14 (1994) 215.
[33] J. Guan, Q. Shen, S. Jin, Y. Lin, Polyhedron 13 (1994) 1695.
[34] A. Hammel, J. Weidlein, J. Organomet. Chem. 388 (1990) 75.
[35] E.O. Fischer, H. Fischer, J. Organomet. Chem. 6 (1966) 141.
[36] W.J. Evans, T.P. Hanusa, J.H. Meadows, W.E. Hunter, J.L. Atwood, Organometallics 6 (1987) 295.
[37] R.D. Shannon, Acta Crystallogr. Sect. A. 32 (1976) 751.
[38] H.J. Heeres, A. Meetsma, J.H. Teuben, R.D. Rogers, Organometallics 8 (1989) 2637.
[39] W. Lamberts, H. Lueken, B. Hessner, Inorg. Chim. Acta 134 (1987) 155.
[40] D. Deng, F. Song, Z. Wang, C. Qian, G. Wu, P. Zheng, Polyhedron 11 (1992) 2883.
[41] J.L. Atwood, W.E. Hunter, A.L. Wayda, W.J. Evans, Inorg. Chem. 20 (1981) 4115.
[42] H. Schumann, H. Lauke, E. Hahn, M.J. Heeg, D. van der Helm, Organometallics 4 (1985) 321.
[43] M.D. Taylor, C.P. Carter, J. Inorg. Nucl. Chem. 24 (1966) 387.